

# Mechanism of Fire Retardancy of Polyurethanes Using Ammonium Polyphosphate

SOPHIE DUQUESNE,<sup>1</sup> MICHEL LE BRAS,<sup>1</sup> SERGE BOURBIGOT,<sup>1,\*</sup> RENÉ DELOBEL,<sup>1</sup> GIOVANNI CAMINO,<sup>2</sup> BEREND ELING,<sup>3</sup> CHRIS LINDSAY,<sup>3</sup> TOON ROELS,<sup>3</sup> HERVÉ VEZIN<sup>4</sup>

<sup>1</sup> Laboratoire de Génie des Procédés d'Interactions Fluides Réactifs, Matériaux, UPRES EA 2698, E.N.S.C.L.-USTL, BP 108, F-59652 Villeneuve d'Ascq Cedex, France

<sup>2</sup> Dipartimento di Chimica Inorganica e Chimica dei Materiali, University of Torino, Torino, Italy

<sup>3</sup> ICI Polyurethanes, Everberg, Belgium

<sup>4</sup> Laboratoire de Chimie Organique et Macromoléculaire, USTL, Villeneuve d'Ascq, France

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**ABSTRACT:** In this work, we studied the mechanism of the fire retardancy of ammonium polyphosphate (APP) in polyurethane (PU). Indeed, according to the limiting oxygen index test, the efficiency of APP in PU coating was proven. On the one hand, thermogravimetric analyses showed that the addition of APP to PU accelerates the decomposition of the matrix but leads to an increase in the amount of high-temperature residue, under an oxidative or inert atmosphere. This stabilized residue acts as a protective thermal barrier during the intumescence–fire retardancy process. On the other hand, spectroscopic analysis of the charring materials using infrared spectroscopy, MAS NMR of the solid state, and ESR enables better understanding of the carbonization process and, consequently, of the intumescence phenomenon. It has been shown that the char resulting from PU consists of an aromatic carbonaceous structure which condenses and oxidizes at high temperature. In the presence of APP, a reaction between the additive and the polymer occurs, which leads to the formation of a phosphocarbonaceous polyaromatic structure. Moreover, this char is strongly paramagnetic. The presence of large radical species, such as a polyaromatic macromolecule trapping free radicals, was demonstrated. Both of these characteristics help to explain the fire-retardant performance of PU/APP. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3262–3274, 2001

**Key words:** coatings; flame retardance; polyurethanes; solid-state structure; thermal properties

## INTRODUCTION

Polyurethane (PU) polymers are used in a large number of forms<sup>1</sup> because of the variety of prod-

ucts which can result from the ingredients of a formulation.<sup>2</sup> Foams, either flexible or rigid, are the most common commercial products. Moreover, PUs are also extensively used as elastomers, adhesives, and coatings.<sup>3</sup> Like the majority of organic materials, PUs are combustible.<sup>4</sup> Consequently, their use is particularly limited in buildings or in transport applications.

A particular way to flame-retard polymers is to use intumescent systems.<sup>5,6</sup> Intumescence is the

Correspondence to: S. Duquesne (s.duquesne@pop.ensc-lille.fr).

\*Present address: Laboratoire de Génie et Matériaux Textiles, Ecole Nationale Supérieure des Arts et Industries Textiles, Roubaix, France.

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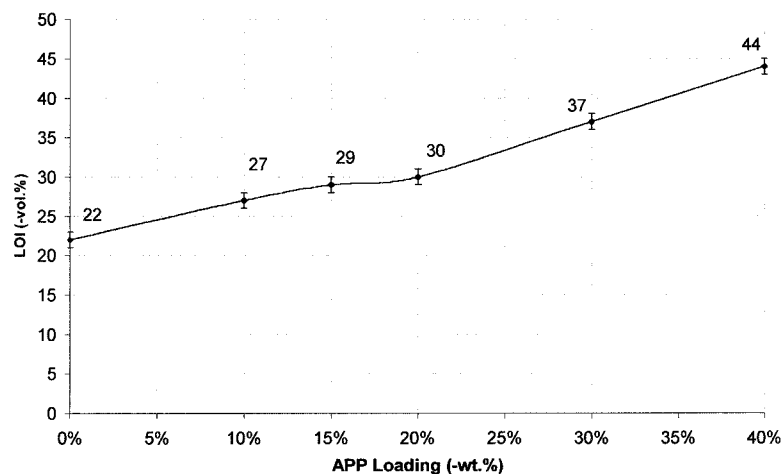


Figure 1 Evolution of the LOI (ASTM D2863/77) values versus APP level in PU.

process in which, in a fire, a suitable combination of various components generates a cellular charred layer on the surface of the material which protects the underlying material from the action of the heat flux or flame and acts as a physical barrier limiting the diffusion of combustible volatile products toward the flame and of oxygen toward the polymer. The proposed mechanism is based on the charred layer acting as a physical barrier, which slows down heat and mass transfer between the gas and the condensed phases.<sup>7,8</sup>

Ammonium polyphosphate (APP) is an effective intumescent fire retardant for several kinds of polymer-based materials<sup>9,10</sup> and, in particular, for PU.<sup>4</sup> It is a high molecular weight chain phosphate. Its efficiency is generally attributed to increase of the char formation through a condensed-phase reaction.

Intumescent PU coatings may be used to protect several kinds of substrates and, in particular, plastics. The use of coatings represents an alternative approach for improving the fire retardancy of polymers. This method should eliminate most disadvantages caused by the incorporation of additives in polymers such as the loss of mechanical properties and processability.

This article investigated the flame-retardant mechanism of APP in a PU coating. As presented in Figure 1, APP is an effective fire retardant for PU. The curve of the limiting oxygen index (LOI) versus APP content shows an increase in the LOI values with the APP level. When adding APP at 40 wt %, the LOI value increases from 22 to 44 vol %. In the first part of the article, the thermal behavior of PU and PU/APP formulations is examined. Then, characterization of the intumes-

cent char is carried out using chemical analyses, infrared spectroscopy, NMR of the solid state, and electron spin resonance (ESR).

## EXPERIMENTAL

### Materials

The raw materials used were polymeric diisocyanate diphenylmethane (Suprasec 2085, ex. I.C.I., Everberg, Belgium) and polyester polyol [poly(terephthalate ester), ex. I.C.I.]. PU coatings were obtained by polycondensation of the isocyanate with the polyol. The molar ratio NCO/OH was fixed equal to 2. APP [(NH<sub>4</sub>PO<sub>3</sub>)<sub>n</sub>, *n* = 700, Clariant Hostaflam AP422 (Sulzbach, Germany), soluble fraction in H<sub>2</sub>O: < 1wt %] was incorporated into PU with a 40 wt % loading.

The initial mixture (monomers/additive) was first carried out using a Turbo Turrax mixer (8000  $\pi$ rad/min). Then, the components were stirred (1000  $\pi$ rad/min) in disposable paper cups (500 mL) at room temperature for 1 min and let to polymerize for 24 h.

These materials (PU and PU/APP coatings) were degraded isothermally at five characteristic heat-treatment temperatures (HTT; 240, 290, 320, 370, and 450°C) during 12 h under an air flow (flow rate = 10<sup>-6</sup> m<sup>3</sup>/s). An intumescent coating was obtained at every temperature and then analyzed using spectroscopic tools.

### Thermal Analyses

Thermogravimetric analyses (TGA) were carried out at 10°C/min under synthetic air or nitrogen

(flow rate:  $5 \times 10^{-7} \text{ m}^3/\text{s}$ , Air Liquide grade) using a Setaram MTB 10-8 microbalance. In each case, the mass of the sample used was fixed at 10 mg and the samples (powder mixtures) were positioned in open vitreous silica pans. The precision of the temperature measurements was  $1.5^\circ\text{C}$  over the whole range of temperatures.

The curves of weight differences between the experimental and theoretical TGA curves are computed as follows:

$$\begin{aligned} M_{\text{poly}}(T): & \text{ TGA curve of PU;} \\ M_{\text{add}}(T): & \text{ TGA curve of APP;} \\ M_{\text{exp}}(T): & \text{ TGA curve of PU/APP;} \\ M_{\text{the}}(T): & \text{ TGA curve computed by linear combination between the TGA curves of PU and APP;} \\ & M_{\text{the}}(T) = 0.6M_{\text{poly}}(T) + 0.4M_{\text{charge}}(T); \\ \Delta(T): & \text{ curve of weight difference;} \\ & \Delta(T) = M_{\text{exp}}(T) - M_{\text{the}}(T). \end{aligned}$$

The  $\Delta(T)$  curve enables observation of an eventual increase or decrease in the thermal stability of the polymer related to the presence of the additive.<sup>11</sup>

### Chemical Analyses

The determination of the amounts of carbon was made by burning the sample in an excess of oxygen at  $1050^\circ\text{C}$ . The quantity of the evolved  $\text{CO}_2$  was then determined by coulometry and was proportional to the total quantity of carbon in the sample.

The quantity of nitrogen was determined by burning the sample in He with 3% oxygen at  $1050^\circ\text{C}$ . The evolved nitrogenated oxides were then reduced to molecular nitrogen, the quantity of which was determined with a catharometer. The quantity of phosphorus was determined by mineralization in an aqueous medium and quantified by plasma emission spectrometry.

### Spectroscopic Analyses

#### NMR of the Solid State

High-resolution NMR spectroscopy of the solids was performed using a Bruker ASX 100 spectrometer at a spinning speed of 5 kHz and using a Bruker probe head equipped with a 7-mm magic-angle spinning (MAS) assembly.  $^{13}\text{C}$ -NMR measurements were performed at 25.2 MHz (2.35 T) with MAS, high-power  $^1\text{H}$  decoupling and  $^1\text{H}$ - $^{13}\text{C}$ -cross polarization (CP). The Hartmann-Hahn

matching condition was obtained by adjusting the power on the  $^1\text{H}$  channel for a maximum  $^{13}\text{C}$  FID signal of adamantane. All spectra were acquired with contact times of 1 ms. It was shown that the intensities of the bands of the samples were maximized under these conditions. A repetition time of 10 s was used for all the samples at all temperatures. Typically, 10,000 scans were necessary to obtain spectra with good signal-to-noise ratios. Tetramethylsilane was used as a reference.

$^{31}\text{P}$ -NMR measurements were performed at 40.5 MHz using MAS. Experiments were carried out with and without  $^1\text{H}$  dipolar decoupling. A repetition time of 450 s was used for all samples because of the long spin-lattice relaxation time for condensed phosphorus species [it is estimated to 90 s (ref. 12)].  $\text{H}_3\text{PO}_4$  in an aqueous solution (85%) was used as a reference.

#### Infrared Spectroscopy

FTIR spectra were recorded using a Nicolet 400D spectrometer in the range  $4000\text{--}300 \text{ cm}^{-1}$ . Samples were ground and mixed with KBr to form pellets. Sixty-four scans were necessary to obtain spectra with good signal-to-noise ratios.

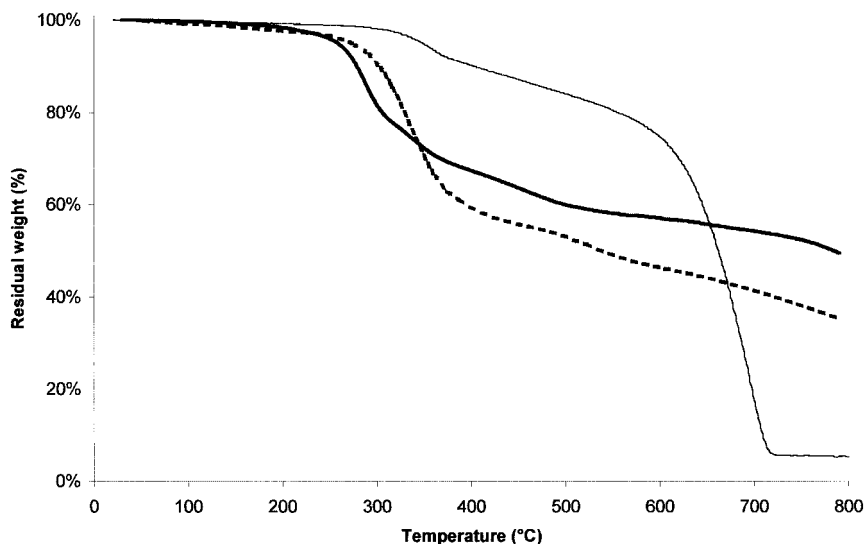
#### Electron Spin Resonance

X-band ESR spectra were recorded with a Bruker ELEXYS 580 spectrometer operating at 9.77 GHz and a 100-kHz modulation frequency at room temperature ( $20^\circ\text{C}$ ). Microwave power was set to 12 mW. Spectra titration was performed using a weak pitch sample at a known concentration of  $10^{13}$  spin per gauss using the double-integration method.

## RESULTS AND DISCUSSION

### Degradation of PU and PU/APP

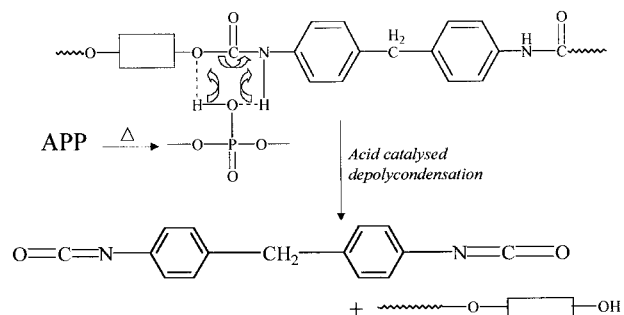
Figure 2 compares the thermogravimetric (TG) curves of PU, APP, and PU/APP under nitrogen. The two degradation steps of APP were previously reported in the literature.<sup>13,14</sup> The first step, which begins around  $300^\circ\text{C}$ , consists essentially of elimination of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , leading to the formation of a highly crosslinked polyphosphoric acid, whereas the second step, at a temperature higher than  $550^\circ\text{C}$ , corresponds to polyphosphoric acid evaporation and/or dehydration to  $\text{P}_4\text{O}_{10}$  which sublimates. In regard to pure PU, a first step of degradation between  $240$  and  $400^\circ\text{C}$ ,



**Figure 2** TGA curves of (---) PU, (—) APP, and (—) and PU/APP under nitrogen.

which has already been investigated,<sup>15</sup> is observed and attributed to the depolycondensation reaction. Then, at higher temperature, the material degrades slowly and a 40 wt % residue is maintained at 800°C. In the presence of APP, the degradation of PU begins at a lower temperature than do the degradations of PU and APP. This suggests that PU and APP react first. An acceleration of the depolycondensation reaction has already been proposed due to acid catalysis by the phosphoric acid<sup>16</sup> as illustrated in Figure 3. The major step of degradation occurs between 240 and 370°C, with a rate of weight loss maximum at 290°C. Between 370 and 500°C, the material presents a low rate of degradation. In the high-temperature range, the amount of residue remains almost constant and equal to 50 wt %.

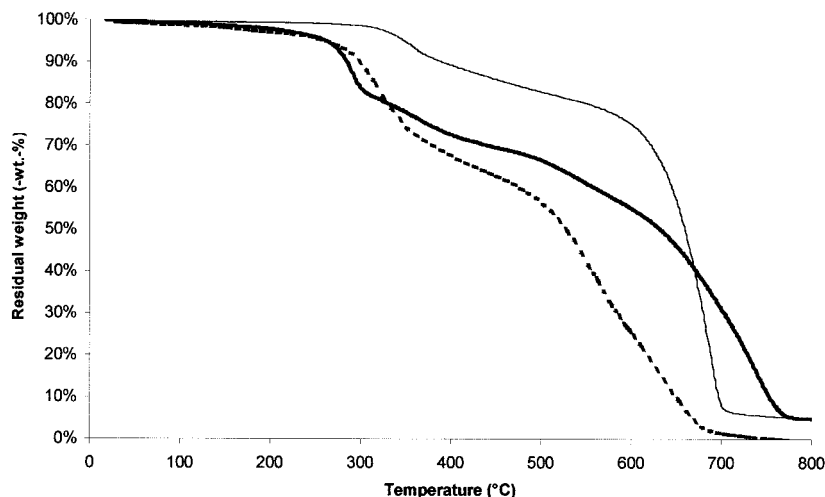
TG curves of PU, APP, and PU/APP under air are compared in Figure 4. Degradation of APP is



**Figure 3** Catalytic action of phosphoric acid on depolycondensation reaction.<sup>16</sup>

similar under air and nitrogen. The TG curve for PU coating shows that the formation of a carbonaceous material under air occurs in two successive steps. The first step starts from 220 to 400°C and the rate of weight loss is maximal at 320°C. The second step of degradation in the temperature range 400–700°C leads to 0 wt % residue. The TG curve of the intumescent material shows a three-step process. The first one, with a peak at about 290°C, may be assigned to the reaction between PU and APP, as previously suggested under nitrogen. Then, a carbonaceous material is formed in the temperature range 320–550°C. This material shows a rapid degradation in the higher-temperature range with formation of a “high-temperature” residue (about 10%). We observed the higher thermal stability of the PU/APP formulation compared to the PU one for a temperature higher than 320°C. This suggests that the addition of APP in PU leads to the formation of a thermally stable material.

The interactions between the polymeric matrix and the additives are shown according to the curve  $\Delta(T)$  (Fig. 5). The behavior is similar under an inert or oxidative atmosphere. First, the weight difference curve is negative between 200 and 500°C under air (600°C under nitrogen), corresponding to the reaction between the polymer and the additive. It confirms the previous discussion on the catalytic action of phosphoric acid on the degradation of PU (Fig. 3). On the other hand, the formation of a stable material in the temperature range 500 (600°C under  $N_2$ )–800°C is ob-

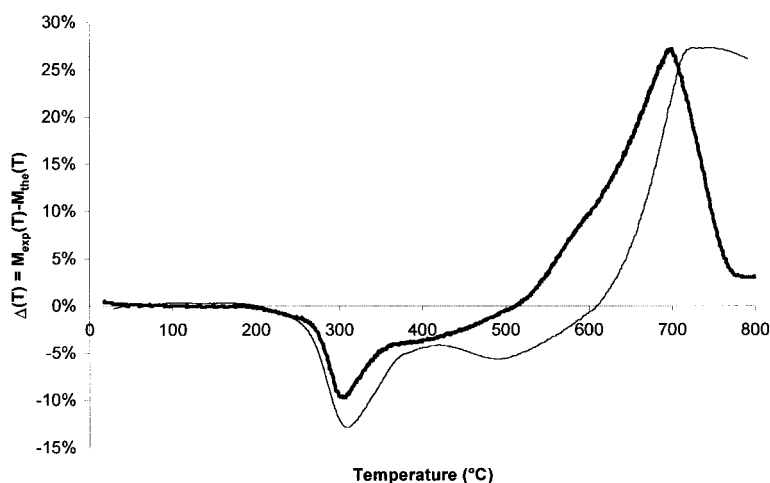


**Figure 4** TGA curves of (---) PU, (—) APP, (—) and PU/APP under air.

served. Consequently, it is obvious that the presence of APP in PU affects its thermal decomposition in several ways, decreasing the initial thermal stability in the earlier stage of the degradation and then leading to the formation of a larger quantity of a high-temperature residue. This aspect seems very interesting in terms of fire retardancy. In fact, a reaction in the condensed phase occurs which stabilizes the residue in the high-temperature range. Consequently, the degradation of the material is lower and the flame resistance of the material increases.

Figure 6 compares TGA curves for PU under air and nitrogen. We observed that oxygen plays a part in the formation of a carbonaceous material stable in the temperature range 350–530°C.

However, at higher temperatures, in air, a complete degradation of the material occurs, whereas in a nitrogen atmosphere, a residue is maintained up to 800°C (30%). The thermooxidative degradation is similar to pyrolysis up to a 30% weight loss. The last step of the degradation under air may be attributed to oxidation of the material, while this step disappears under nitrogen. This stabilization phenomenon under air may be explained by a competition between a reaction of the material with oxygen, which leads to an increase in the weight, and an oxidation process, which leads to a decrease in the mass. In the case of the PU/APP formulation, Figure 7 confirms that oxygen plays a part in the formation of a stable carbonaceous material between 300 and 585°C



**Figure 5**  $\Delta T$  curve of the formulation PU/APP under (—) air and (---) nitrogen.

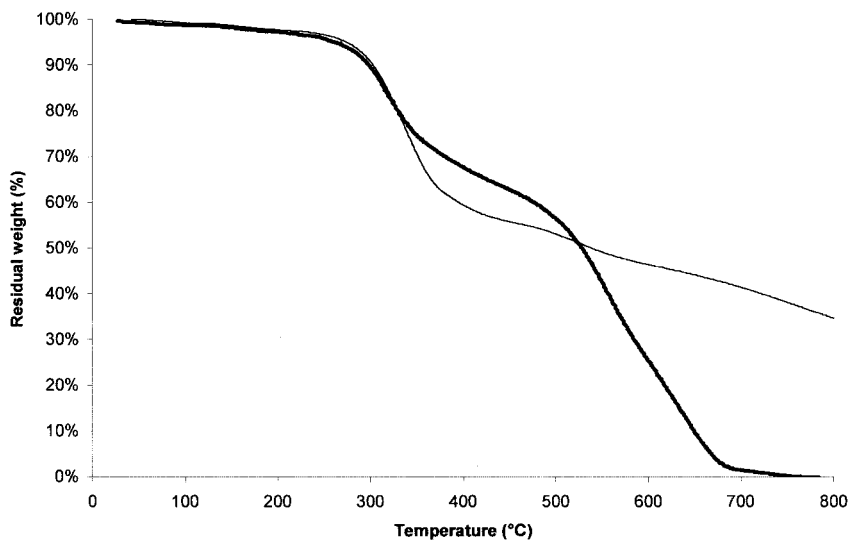


Figure 6 TG of PU under (—) air and (---) nitrogen.

and then in the degradation of the material at higher temperature. Consequently, in both cases, it seems that oxygen enhances the thermal stability during the first step of the degradation, but above this step, the rate of the weight loss increases and the degradation becomes complete for the pure polymer and leads to the formation of a stable residue in the high-temperature range with PU/APP.

#### Spectroscopic Characterization of Chars

To simulate the evolution of the intumescence structure, five characteristic temperatures (heat-treatment temperature: HTT) were determined according to the TG curves:

- 240°C corresponds to the beginning of the first step of degradation, that is, the development of the intumescence.
  - 290°C/320°C correspond to the maximum weight loss rate of the first step respectively for PU/APP and PU
  - 370°C permits the study of an intermediate stage
  - 450°C represents the end of the first step, that is, the degradation of the intumescent shield.
- } that is, the stabilization of the char.

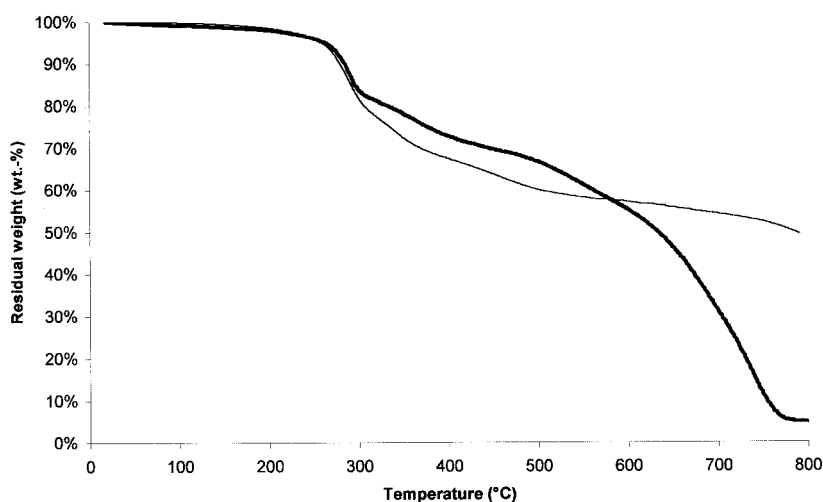


Figure 7 TG curves of PU/APP under (—) air and (---) nitrogen.

**Table I** Description of Isothermally Heat-treated Samples

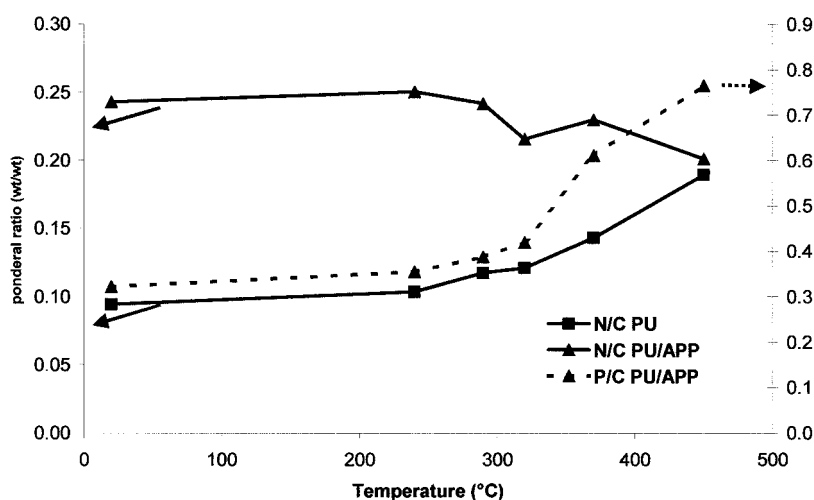
HTT (°C)	Residual Mass (wt %)	Resulting Material	Blowing of the Material (vol %)
240	89	Tough and bright, black material	8
290	85	Tough, black material	13
320	79	Tough, black material	21
370	71	Tough, black material	35
450	34	Crumbly, black material	5

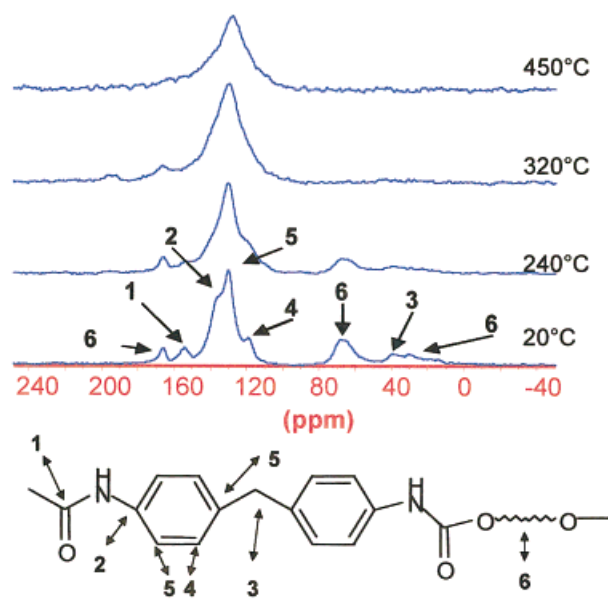
It is interesting to study the residue formed after isothermal treatment (12 h) under air at these characteristic temperatures.

Some characteristics of these residues are summarized in Table I for the PU/APP formulation. The formation and the chemical structure of the products of the degradation of PU and PU/APP were studied using spectroscopic tools to better understand the mechanism of protection.

The residues were first characterized by elemental analyses. Figure 8 presents the changes of the ratios of weight percentages N/C and P/C for pure PU and PU/APP coatings. As far as PU is concerned, the ratio N/C increases from 240°C. Consequently, we may assume that nitrogen may be implicated in heat-resistant structures. In the case of PU/APP, the N/C ratio slightly decreases from 240 to 450°C. In that case, there are two sources of nitrogen: PU (for 40 wt %) and APP (for 60 wt %). When heated, APP leads to the evolution of water and ammonia, which is very reactive. If no reaction occurs between PU and APP, the N/C ratio should be similar for PU and PU/

APP for high HTT. However, we note that the ratio N/C is always higher for PU/APP than for PU whatever the HTT is. Consequently, it may be assumed that the ammonia reacts with carbonaceous species to form stable nitrogenated species. Bourbigot et al. previously demonstrated that this kind of reaction may occur in the thermooxidative degradation of the APP/PER mixture.<sup>17</sup> The P/C ratio of the formulation PU/APP increases from 240 to 450°C and the weight percent of P contained in the residue increases (from 14 wt % at 20°C to 20 wt % at 450°C). This means that in the high-temperature range stabilization of the phosphorus species is favored compared to the carbonaceous species. Consequently, the interaction between the polymer and the additive leads to the stabilization of the phosphorus species in the protective shield and, consequently, to a stabilization of the matrix in the presence of APP as observed on the TG curve. This was already observed in intumescent char.<sup>18</sup> The study by solid-state NMR was carried out to characterize the chemical groups of the carbonaceous and

**Figure 8** N/C and P/C ratios versus HTT for PU and PU/APP coatings.



**Figure 9** CP-DD-MAS  $^{13}\text{C}$ -NMR spectra of PU coating at the HTT indicated. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

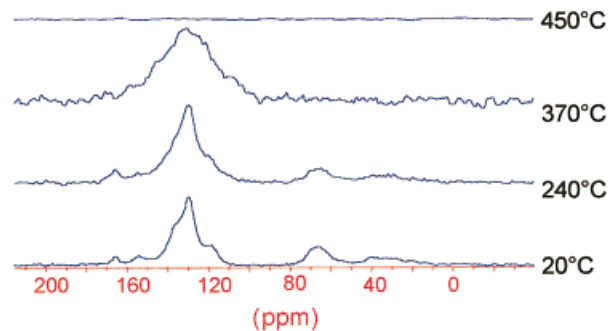
phosphorus species obtained during the degradation.

The CP-DD-MAS  $^{13}\text{C}$ -NMR spectra and their assignments<sup>19–23</sup> are presented in Figure 9 for the virgin polymer. The band at 154 ppm, which is characteristic of the urethane function, disappears when the temperature increases from 240 to 320°C. Consequently, it suggests, as previously observed using TGA, that the carbonization process begins between 240 and 320°C. At each HTT, an intense peak is observed around 130 ppm, which implies the presence of several nonmagnetically equivalent aromatic carbons in the material. At ambient temperature, this band is well defined and three components are observed. They correspond to the different carbons of the aromatic cycles of polymeric diisocyanate diphenylmethane (PMDI). At higher temperature, this band is broad and may be attributed to the presence of several types of aromatic and polyaromatic species.<sup>24,25</sup> The width of this peak increases with the temperature and a trail toward the lower field is observed. This phenomenon corresponds to the condensation and the oxidation of the aromatic species. The band at 165 ppm, attributed to the ester function of the polyol, is observed to 320°C. As a consequence, we may assume that the degradation of the polyol occurs at higher temperature than the one of the ure-

thane bonds. On the other hand, a peak of low intensity at 194 ppm is observed for an HTT of 320°C. This peak may be assigned to the ketone function. In fact, polyester, when degrading, leads to the formation of such species.<sup>26</sup> Moreover, the oxidation of the degraded matrix may also lead to the formation of ketonic groups via a radical mechanism. Consequently, PU, which is a char-forming polymer, forms, when degrading, a carbonaceous layer at the surface of the material. We demonstrated that this layer is formed by condensed polyaromatic species partially oxidized.

Figure 10 presents CP-DD-MAS  $^{13}\text{C}$ -NMR spectra of the PU/APP coating versus the HTT. At ambient temperature, spectra are similar with or without additives. So, the addition of APP in the formulation does not modify the carbon structure of the PU. Between room temperature and 370°C, the spectra present a broad band around 130 ppm, implying the presence of aromatic and/or polyaromatic carbons in the material. The  $^{13}\text{C}$  signal disappears for an HTT of 450°C, whereas carbon has been detected by chemical analyses. We may explain this phenomenon by the presence of free radicals trapped in the aromatic carbonaceous structure of the material, which, consequently, escape detection. Indeed, the reduction in the resolution of the  $^{13}\text{C}$  signal has been directly related, according to the work of Ganapathy and Bryan,<sup>27</sup> to the anisotropy of the paramagnetic susceptibility of the aromatic compounds. In the case of paramagnetic materials, this anisotropy is large and, consequently, leads to a disappearance of the  $^{13}\text{C}$  signal.

An ESR study confirmed this assumption and gives additional information on the carbonaceous structure. The signal is assigned to free radicals



**Figure 10** CP-DD-MAS  $^{13}\text{C}$ -NMR spectra of PU/APP coating at the HTT indicated. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Table II** Fraction of Radical Carbon Atoms Contained in Intumescent Shield at Different HTTs

HTT (°C)	240	290	320	370	450
$C^*/C_{\text{tot}} \times 10^3$	0.026	0.082	1.03	1.12	0.557

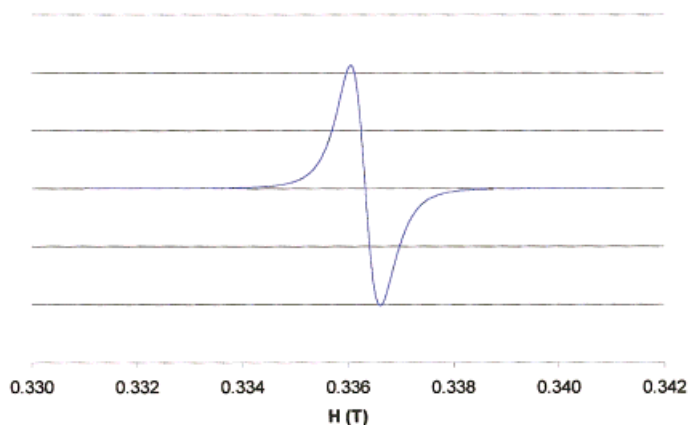
“trapped” in a polyaromatic structure<sup>28</sup> which may result from a charring process of the material. The ratio of the free-radical carbons (normalized relative volumic amount) to the total number of carbon  $C^*/C_{\text{tot}}$  (Table II) is particularly high for HTTs of 320 and 370°C and is of the same order of previous values obtained for PP/APP-PER/4A.<sup>7</sup> We may assume that up to 320°C radicals are created by the formation of polyaromatic species or are associated to the formation of oxidized species. In this first range of temperature, the development and the stabilization of the charring shield occurs. At 450°C, the concentration of radicals is still high but decreases. This may be attributed to a competition between the chain-breaking process and a condensation phenomenon of the aromatic species. It corresponds to the degradation of the intumescent shield.

On the other hand, the ESR spectroscopy study gives access to the spectroscopic splitting factor  $g$  and to the resonance line shape. Typical examples of the signals are presented in Figure 11, and the corresponding fit analyses of the integrated signal, in Figure 12.

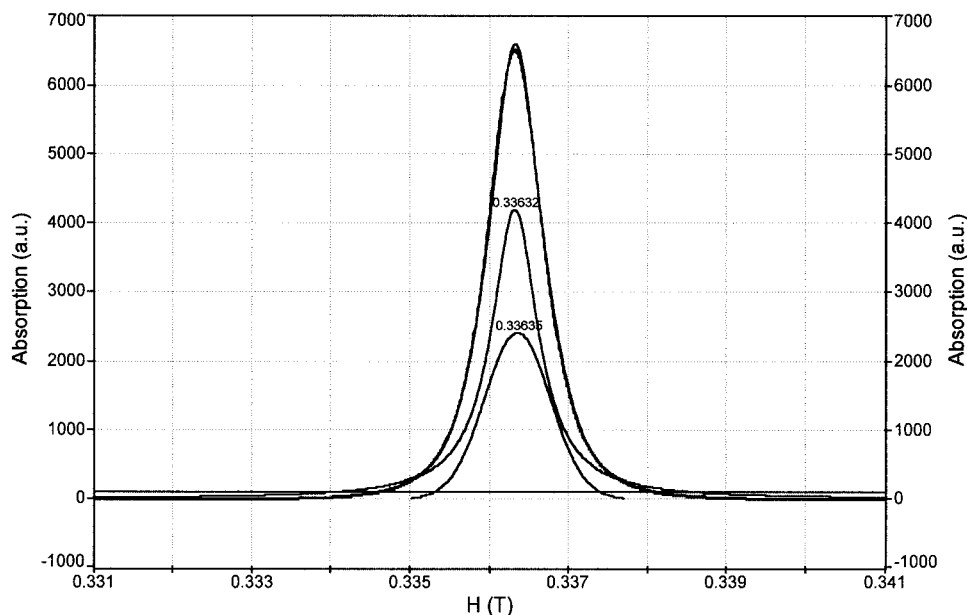
Characteristic data of the ESR spectra of PU/APP coatings heat-treated at characteristic HTTs are reported in Table III. The residues resulting

from the isothermal degradation of the PU/APP formulation show a splitting factor  $g$  around 2.0060. These high values of  $g$  strongly suggest the presence of oxygen in the free radical.<sup>29</sup> The line shape gives information about the interaction between a spin system and its environment. ESR lines with a homogeneous Lorentzian shape are explained by individual “spin packets” in which all the free-radical spins behave cooperatively like a single-spin system. It may be assigned to radical species that are large and that, consequently, have few protons. Lines with an inhomogeneous Gaussian line shape correspond to the envelope of several small radical species. In that case, resonance of all the spin systems does not occur simultaneously. A comparatively high number of protons and/or of chemical functions (such as alkyl or aryl groups and oxidized species) bound to the carbon structure are also present. For all the HTTs, the Lorentzian function is the major one. Consequently, the carbonization process involves large radical species, probably a polyaromatic macromolecule which has trapped free radicals. Moreover, the width of the peak is generally narrow ( $<10 \times 10^{-5} T$ ), which characterizes large radicals resulting in small electron-proton interactions mainly responsible for the line width.

The MAS <sup>31</sup>P-NMR spectra and their assignments are presented in Figure 13. At 230°C, the spectrum presents a twin peak which may be assigned to the P—OH link (−22.4 ppm) or to the PO<sup>−</sup>NH<sub>4</sub><sup>+</sup> species (−24 ppm) in condensed phosphate species.<sup>30,31</sup> These bands are characteristic of pure APP. When the temperature increases, one can observe that it degrades and reacts. In-



**Figure 11** ESR spectrum of PU/APP heat-treated at 450°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 12** Integrated ESR spectrum (one Lorentzian and one Gaussian function) of PU/APP heat-treated at 450°C.

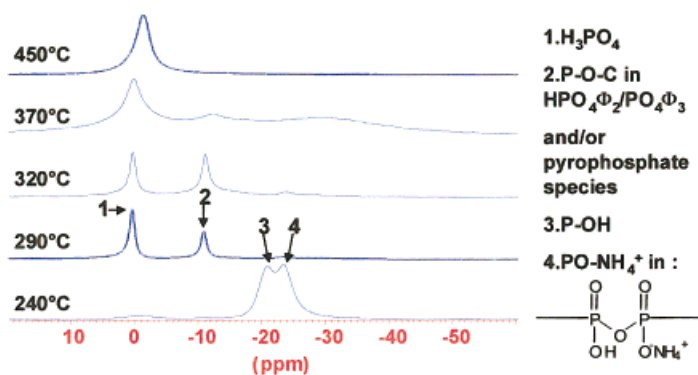
deed, we observed that, from 290°C, the doublet assigned to polyphosphate chains disappears and new peaks around  $-11$  ppm and  $0$  ppm appear. As spectra carried out with and without  $^1\text{H}$  dipolar decoupling are similar, the band around  $-11$  ppm may be attributed to orthophosphate groups linked to aromatic cycles and/or to pyrophosphate species. The band at  $0$  ppm corresponds to orthophosphoric acid. So, we may assume that APP reacts first with the PU matrix with the consequent formation of an aromatic phosphocarbonaceous structure with  $\text{P—O—C}$  bridges. At higher temperature, the intensity of the bands around  $-11$  ppm decreases significantly.  $\text{P—O—C}$  bridges are broken in relation to the condensation

**Table III** Characteristics of the ESR Spectra of Chars Resulting from the Thermal Treatment of PU/APP Coating

HTT (°C)	% Area of Functions		Width (T)	g
	Lorentz	Gauss		
240	74	26	6.72	2.0065
290	71	29	4.89	2.0061
320	93	7	1.48	2.0059
370	62	38	4.19	2.0060
450	59	41	5.59	2.0059

of the aromatic species, as  $^{13}\text{C}$ -NMR and ESR studies have demonstrated. At 370°C, we observe a broad peak of low intensity at  $-28$  ppm. We may suggest the formation of a condensed phosphate species (such as polyphosphoric acid) according to the fact that it was previously reported that the degradation of APP leads to the formation of such a structure.<sup>32</sup>

An IR study was carried out to confirm the hypothesis deduced from the NMR spectroscopy. Comparison of the spectrum of PU with and without additives (Fig. 14) proves that APP does not modify the chemical structure of the polymer. The band around  $2266\text{ cm}^{-1}$  is attributed to unreacted isocyanate. Consequently, the reaction of polycondensation is not total. The spectra versus HTT are presented in Figure 15. Significant modifications of the spectrum are observed from 290°C. Consequently, as suggested by the TGA analysis, the carbonization process occurs between 240 and 290°C. The  $850\text{--}1350\text{ cm}^{-1}$  spectral region corresponds to the absorption range for  $\text{P—O}$  bands and allows us, on the one hand, to characterize the phosphate species and, on the other hand, to prove the formation of a phosphocarbonaceous structure. At every temperature, the spectra present broad bands between  $1100$  and  $1300\text{ cm}^{-1}$  assigned to  $\text{P—O—C}$  bonds in phosphate-carbon complexes.<sup>33</sup> The additional broad bands at about  $1000\text{ cm}^{-1}$  may be assigned to symmetric vibra-



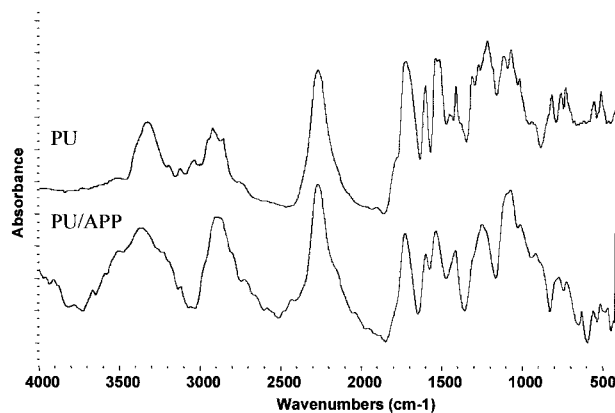
**Figure 13** MAS/DD  $^{31}\text{P}$ -NMR for PU/APP coating at the HTT indicated. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

tion modes of  $\text{PO}_2$  and  $\text{PO}_3$ , which are characteristic of phosphocarbonaceous complexes. These results demonstrate, therefore, the formation of a phosphocarbonaceous structure from 290°C which is maintained to 450°C. Moreover, it is of interest to note the presence of aliphatic carbon (around  $2950\text{ cm}^{-1}$ ) to 450°C, which had not been detected using  $^{13}\text{C}$ -NMR. This was already observed by Bourbigot et al.<sup>34</sup> and attributed to a blocking of the CP process according to Suwelack<sup>35</sup> and Ollivier and Gerstein.<sup>36</sup> In fact, they studied the intensity of aliphatic carbon bands for a given pitch in the conditions of rotation at the magic angle and they observed its decrease and sometimes its disappearance. They considered that the motion of sufficiently low frequency coupled with MAS results in complete decoupling of the proton-carbon dipolar interaction. On the other hand, we may propose that the quantity of aliphatic carbon decreases when the HTT increases. Finally, the double bands which appear

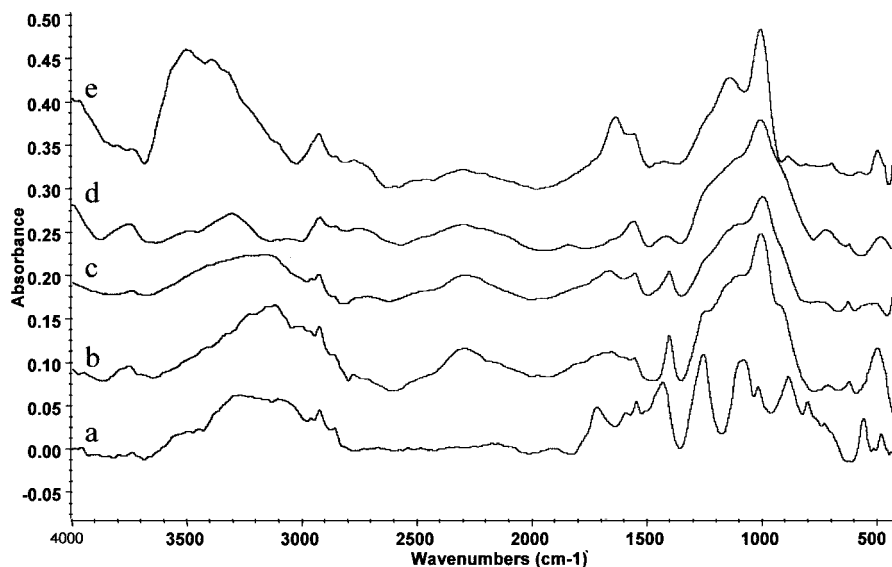
between  $1700$  and  $1500\text{ cm}^{-1}$  may be assigned to  $\text{C}=\text{C}$  and/or  $\text{C}=\text{N}$  stretching vibrations in aromatic compounds, which confirms the results obtained in previous analysis.

### General Discussion

Regarding these results, we may explain why the carbonaceous layer forms from PU/APP has fire-retardant properties of interest. The role of APP is clearly demonstrated by the spectroscopic study of the residues obtained by isothermal treatment at characteristic temperatures. The formation of a phosphocarbonaceous structure via reaction between the polymer and the additive stabilizes the material and therefore favors the fire-proofing properties. Indeed, when pure PU degrades, it develops a carbonaceous shield with a structure consisting of polyaromatic species which creates a rigid material. The corresponding rigid domain is proposed as an initiator for the formation of cracks in the coating. As a consequence, encapsulated gases (products of the degradation of the polymer) evolve and contribute as fuel to the flame. In the case of the PU/APP formulation, the char layer is composed of condensed aromatic species bridged by  $\text{P}-\text{O}-\text{C}$  bonds. Such a structure can accommodate the stress due to the internal pressure of gases of degradation and, consequently, can retard the formation and propagation of cracks. As a consequence, the stabilization of polymer links that are able to bridge polyaromatic species via the phosphate group may provide the mechanical properties of interest for the intumescent coating. They give flexibility to the carbonaceous shield,<sup>18</sup> which, in the conditions of a fire, retards the creation and propagation of cracks in which the air can diffuse to the



**Figure 14** IR spectra of PU and PU/APP coatings at 20°C.



**Figure 15** IR spectra for PU/APP coating at the HTT indicated (a: 240°C; b: 290°C; c: 320°C; d: 370°C; e: 450°C).

polymeric matrix, causing evolution of small molecules that can act as fuel for the fire.

## CONCLUSIONS

In this work, we investigated the mechanism of fire retardancy of APP in PU. The study of the carbonaceous coating obtained for the PU/APP formulation by isothermal treatments clearly shows the role played by APP in the structure to provide the desired fire-proofing properties. Although the PU decomposition reaction is accelerated in the presence of APP, it is clear that more char is formed. This char presents a phosphocarbonaceous structure which is thermally more stable than is the carbonaceous structure obtained for PU. The intumescent shield traps polymer fragments under organic phosphates and limits the depolymerization, that is, the evolution of small flammable molecules able to feed the flame. On the other hand, the addition of APP to PU leads to an increase in the amount of high-temperature residue which acts as a protective thermal barrier during the fire-retardancy process. The structure of this consists of stacks of polyaromatic species linked principally by phosphocarbonated bridges. These bridges provide the dynamic properties of interest to the structure, which is then able to accommodate the stresses. Moreover, an ESR study showed the presence of free radicals in the protective coating formed in

presence of APP in PU. The presence of radicals species have been proposed as contributing to the fire-retardancy process.

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## REFERENCES

1. Woods, G. *The ICI Polyurethanes Book*, 2<sup>nd</sup> ed.; ICI Polyurethanes and Wiley: Chichester, 1990.
2. Hatat, D. In *Techniques de l'ingénieur; Les Techniques de l'ingénieur*: Paris, France, 1995; Vol. AM2, A 3 425.
3. *Encyclopedia of Chemical Technology*; Kirk, R. E.; Othman, D. F., Eds.; Wiley-Interscience: New York, 1997; Vol. 24, p 695.
4. Papa, A. J. In *Flame Retardancy of Polymeric Materials*; Kuryla, W. C.; Papa A. J., Eds.; Marcel Dekker: New York, 1975; Vol. 3, p 1.
5. Vandersall, H. L. *J Fire Flam* 1971, 2, 97.
6. Camino, G. In *Actes du Premier Colloque Franco-phonie sur l'ignifugation des Polymères*; J. Martel: Saint Denis, France, 1985; p 36.
7. Bourbigot, S.; Le Bras, M.; Delobel, R.; Decressain, R.; Amoureux, J. P. *J Chem Soc Faraday Trans* 1996, 92, 149.
8. Mamleev, V. Sh.; Gibov, K. M. In *Fire Retardancy of Polymers: The Use of Intumescence*; Le Bras, M.; Camino, G.; Bourbigot, S.; Delobel, R., Eds.; The Royal Chemical Society: Cambridge, 1998; p 113.

9. Siat, C.; Bourbigot, S.; Le Bras, M. In *Recent Advances in Flame Retardancy of Polymeric Materials*; Lewin, M., Ed.; BCC: Norwalk, CT, 1997; Vol. 7, p 318.
10. Mount, R. A.; Pysz, J. F. *Proc Int Conf Fire Saf* 1991, 16, 203.
11. Delobel, R.; Le Bras, M.; Ouassou, N.; Alistiqsa, F. *J Fire Sci* 1990, 8(2), 85.
12. Le Bras, M. Thèse Doctorat es Sciences Physiques, University of Lille, 1997.
13. Camino, G.; Costa, L.; Trossarelli, L. *Polym Degrad Stab* 1984, 6, 243.
14. Zhang, J.; Horrocks, A. R.; Hall, M. E. *Fire Mater* 1994, 18, 307.
15. Camino, G.; Duquesne, S.; Delobel, R.; Eling, B.; Lindsay, C.; Roels, T. In *Proceedings of the American Chemical Society—Division of Polymeric Materials: Science and Engineering*, Washington, DC, Fall Meeting, 2000; Vol. 83, p 42.
16. Grassie, N.; Zulfiqar, M. In *Developments in Polymer Stabilisation*; Scott, G., Ed.; Applied Science: 1978; Vol 1, p 197.
17. Bourbigot, S.; Le Bras, M.; Gengembre, L.; Delobel, R. *Appl Surf Sci* 1994, 81, 299.
18. Bourbigot, S.; Le Bras, M.; Delobel, R.; Bréant, P.; Trémillon, J. M. *Carbon* 1995, 33, 283.
19. Maciel, G. E.; Sullivan, M. J.; Petrakis, L.; Grandy, D. W. *Fuel* 1982, 61, 411.
20. Hasan, M. U.; Ali, M. F.; Bukhari, A. *Fuel* 1983, 62, 518.
21. Earl, W. L.; Vanderhart, D. L. *J Magn Reson* 1982, 48, 35.
22. Supaluknari, S.; Burgar, I.; Larkins, F. P. *Org Geochim* 1990, 15, 509.
23. Duncan, M. *J Phys Chem Ref Data* 1987, 16, 125.
24. Grint, A.; Proud, G. P.; Poplett, I. J. F.; Bartle, K. D.; Wallace, S.; Matthews, R. S. *Fuel* 1989, 68, 1490.
25. Maciel, G. E.; Bartuska, V. J.; Miknis, F. P. *Fuel* 1979, 58, 391.
26. Grassie, N.; Scott, G. In *Polymer Degradation and Stabilisation*; Grassie, N., Ed.; Cambridge University: Cambridge, UK, 1988; p 34.
27. Ganapathy, S.; Bryan, R. G. *J Magn Reson* 1986, 70, 149.
28. Singer, L. S.; Lewis, I. C.; Rifle, D. M. *J Chem Phys* 1987, 91, 2408.
29. Lewis, I. C.; Singer, L. S. *J Chem Phys* 1981, 85, 354.
30. Van Wazer, J. R.; Callis, C. F.; Shoolery, J. N.; Jones, R. C. *J Am Chem Soc* 1956, 78, 5715.
31. Duncan, T. M.; Douglass, D. C. *J Chem Phys* 1984, 87, 339.
32. Bugajny, M.; Bourbigot, S.; Le Bras, M.; Delobel, R. *Polym Int* 1999, 48, 264.
33. Mc Kee, D. W.; Spiro, C. L.; Lamby, E. J. *Carbon* 1984, 22, 285.
34. Bourbigot, S.; Le Bras, M.; Delobel, R. *Carbon* 1993, 31, 1219.
35. Suwelack, D.; Rothewell, W. P.; Waugh, J. S. *J Chem Phys* 1980, 73, 2559.
36. Ollivier, P.; Gerstein, B. C. *Carbon* 1984, 22, 409.