Thermal Degradation and Pyrolysis Study of Phosphorus-Containing Polysulfones

Oana Petreus,[1] Gabriela Lisa,[2] Ecaterina Avram,[1] Dan Rosu[1]

[1]*Petru Poni Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, 700487 Iasi, Romania*
[2]*Faculty of Chemical Engineering, Gheorghe Asachi Technical University, 71A Dmitrie Mangeron, 700050 Iasi, Romania*

ABSTRACT: This article deals with the thermal decomposition behavior of a polysulfone containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide versus the initial chloromethylated polysulfone under an inert atmosphere and in air. Thermogravimetric characteristics from thermogravimetry and differential thermogravimetry data revealed important differences related to the employed atmosphere, the types of substituted functional groups, or the degree of substitution. The introduction of the 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide pendent group into polysulfone enhanced the thermal stability of the initial chloromethylated polysulfone in both an inert atmosphere and air. Thermal degradation in nitrogen consisted of one degradation step, whereas thermooxidative degradation in air involved more steps. In air, the degradation mechanism was more complex. The volatile products and solid residues that resulted after pyrolysis in an inert atmosphere and in air were analyzed with Fourier transform infrared and mass spectrometry. Environmental scanning electron microscopy showed that the char residues had different morphologies, which suggested that a more compact structure led to better resistance to heat and oxygen. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3233–3241, 2011

Key words: degradation; FTIR; thermal properties; thermogravimetric analysis (TGA)

INTRODUCTION

Aromatic polysulfones (PSFs) and their derivatives represent a family of thermoplastic engineering polymers possessing remarkable thermal stability, excellent strength and flexibility, high glass-transition temperatures, and good film-forming properties. Despite these qualities, the hydrophobic nature of PSFs incites great interest with respect to their chemical modification. Among these polymers, Udel PSF seems to be more suitable for functionalization with different reactive groups (especially chloromethyl groups) because it can be readily modified by a substitution reaction with various nucleophilic reactants.[1–4]

In a previous article,[5] we reported the synthesis and characterization of PSFs containing phosphorous pendent groups that were started from chloromethylated polysulfone (CMPS) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). A preliminary study of their thermal stability in nitrogen was performed with respect to the thermal stability of CMPS. The incorporation of phosphorous pendent groups increased the thermal stability in comparison with that of chloromethylated samples, whereas a slight decrease was observed with an increase in the substitution degree. The decomposition residue was higher for a PSF with a higher content of phosphorous groups. Moreover, the thermal degradation in nitrogen was quite different from the usual thermooxidative behavior of phosphorus-containing polymers.[6] Different polymers that contain phosphorous moieties in the main chain or as pendent side groups belong to the flame-resistant class of materials.[7–11]

When exposed to a flame, polymers undergo pyrolysis, which produces flammable volatiles and different crosslinking reactions in a condensed state. These reactions, influenced by the structure of the polymers, are strongly affected by the position, concentration, or structure of the phosphorous flame-retardant groups. Some articles on the thermal stability of phosphorus-containing polymers concluded that, with respect to flame retardancy, phosphorus acts in both condensed and gas phases.[12,13]

This article reports a detailed study of the thermal decomposition and pyrolysis of some PSFs containing phosphorous pendent groups under inert and oxidative atmospheres; the dependence of structure–thermostability–degradation mechanisms was determined. Some connections with fire resistance were also made.

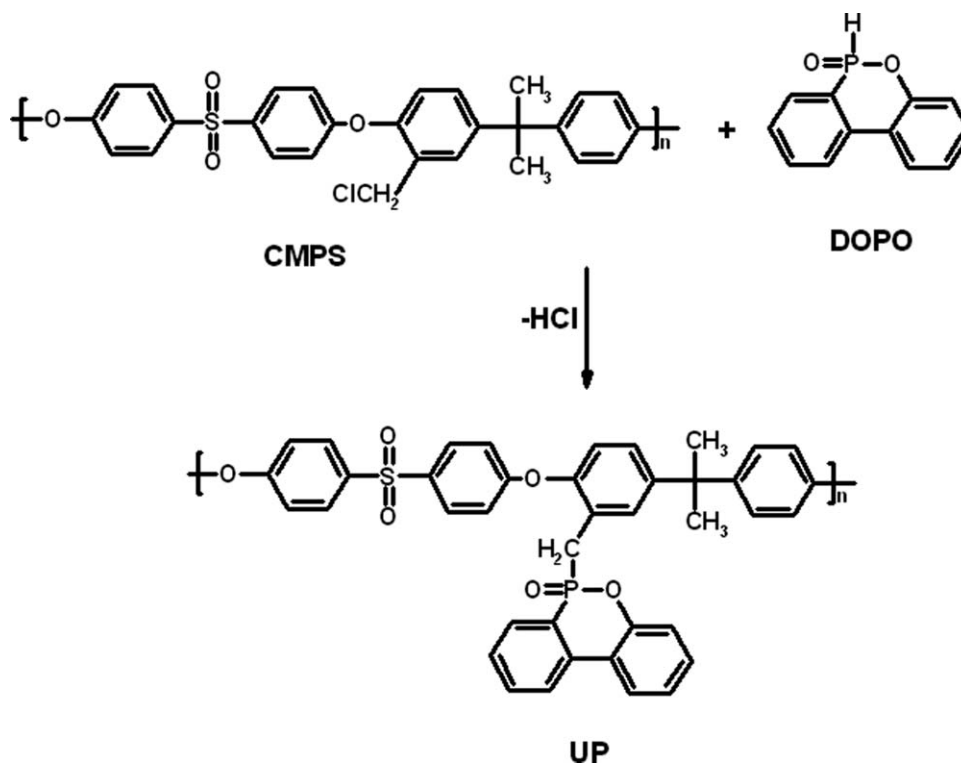*Correspondence to:* O. Petreus (opetreus@yahoo.com).

Figure 1 Reaction of CMPS with DOPO.

EXPERIMENTAL

Materials

Phosphorus-containing PSFs with different degrees of substitution (UP-4, UP-6, and UP-10) were prepared at 170°C under nitrogen for 6 h through the reaction of CMPS (CMPS-4, CMPS-6, and CMPS-10) with DOPO with a large excess of a phosphorous reactant (Fig. 1).

The resultant crude solid was dissolved in chloroform, precipitated in anhydrous methanol, and, after drying, Soxhlet-extracted with methanol for several days to remove the excess of DOPO. The full experimental details for the synthesis and characterization of the obtained PSF have been reported elsewhere.[5] Some characteristics of the obtained phosphorus-containing PSFs are listed in Table I. Elemental analyses for phosphorus were performed by the molybdenum blue method; the chlorine content was determined by the modified Schöninger method.[14]

Measurements

Thermogravimetric (TG) analysis

TG analysis was performed under a nitrogen flow (20 cm^3/min) and in air at a heating rate of 10°C/min from 25 to 700°C with a Mettler-Toledo TGA/SDTA 851 apparatus. The initial mass of the samples was 3–5 mg. The operating parameters were kept constant for all samples so that comparable data could be obtained. The processing of the curves for

TABLE I
Characteristics of Phosphorus-Modified PSFs

Sample	Elemental composition (%)												Molar degree of substitution	Structural unit weight
	C		H		S		O		Cl		P			
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found		
UP-4[a]	72.60	72.50	4.77	4.90	5.69	5.74	13.04	13.59	0.40	0.41	3.06	2.87	0.62	491.5
UP-6[b]	71.35	71.30	4.70	4.69	5.26	5.23	14.13	14.40	0.49	0.45	3.96	3.42	0.74	569.4
UP-10[c]	71.38	71.14	4.10	4.34	4.77	4.52	13.80	13.70	0.4	0.35	5.99	6.03	1.30	975

[a] CMPS with a molar degree of substitution of 0.56 was replaced by DOPO (UP-4).
[b] CMPS with a molar degree of substitution of 0.90 was replaced by DOPO (UP-6).
[c] CMPS with a molar degree of substitution of 1.53 was replaced by DOPO (UP-10).

the determination of the thermal characteristics of the samples under study was undertaken with the help of STAR software from Mettler-Toledo; for the separation of thermal decomposition stages, both TG and differential thermogravimetry (DTG) curves were considered.

Characterization of the volatile pyrolysis products

Evolved gas analysis was performed with a TG/ differential scanning calorimetry/Fourier transform infrared (FTIR)/mass spectrometry (MS) system (model STA 449 F I Jupiter, Netzsch, Germany) coupled to a Vertex 70 FTIR spectrometer (Netzsch) and a QMS 403C Aëolos mass spectrometer (Netzsch). Samples (10 mg) were heated from 25 to 600°C at a heating rate of 10°C/min under a flow of helium (flow rate = 50 mL/min) in an open Al_2O_3 crucible. The transfer line to FTIR, which had an internal diameter of 1.5 mm, was heated at 190°C. The spectra were obtained at a spectral resolution of 4 cm^{-1} over the 400–4000-cm^{-1} range. The transfer line to the QMS 403C MS spectrometer was made from a quartz capillary with an internal diameter of 75 μm, and was heated to 300°C. The mass spectra were obtained after the electron impact mode was applied at an electron energy level of 70 eV. Data were scanned in the m/z = 1–300 range, the measuring time for each cycle being 150 s.

Characterization of the solid pyrolysis products

Pyrolysis residues from the TG experiments, collected at various weight losses, were subsequently analyzed by FTIR spectroscopy with a Vertex 7 spectrometer. The FTIR device was equipped with atmospheric compensation by the software. In the experiments performed in an inert atmosphere, the pyrolysis residues were collected only at 600°C at the end of the process. For experiments performed in air, samples (50 mg) were separately heated in a Ney Vulcan 3-130 furnace (United States) up to 300, 450, 500, or 600°C at a heating rate of 10°C/min. Each pyrolysis residue was collected, and the FTIR spectra were recorded on the Vertex 7 spectrometer with KBr pellets.

The PSF, CMPS, and UP-6 residues, collected after pyrolysis in air at 600°C, were examined with an environmental scanning electron microscope (Quanta 200) at 30 kV with secondary electrons in a low vacuum. Scanning electron microscopy (SEM) studies were performed with samples fixed on copper supports. The Quanta 200 microscope was equipped with an energy-dispersive X-ray system for qualitative and quantitative analysis and elemental mapping.
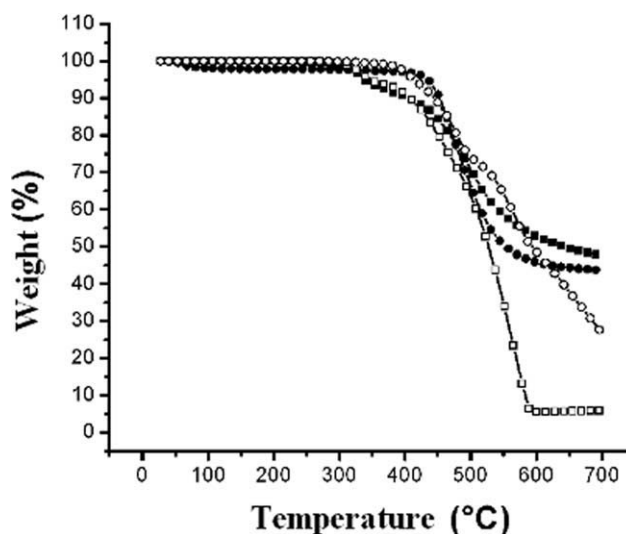

Figure 2 TG curves for the initial CMPS-6 and UP-6 in different atmospheres: CMPS-6 in (■) nitrogen and (□) air and UP-6 in (●) nitrogen and (○) air.

RESULTS AND DISCUSSION

TG analysis

The thermal and thermooxidative stability of the samples was evaluated by dynamic TG analysis in nitrogen gas or an air atmosphere at a heating rate of 10°C/min.

A comparison of the TG curves for the initial CMPS-6 and UP-6 in different atmospheres is presented in Figure 2.

The TG data show that CMPS-6 was less stable then phosphorus-modified UP-6 in both nitrogen and air atmospheres. The decomposition residue was slightly enhanced in a nitrogen atmosphere for CMPS-6 in comparison with UP-6, but it was strongly reduced in air. For UP-6, the degradation paths were quite similar in air and nitrogen until 475°C, after which the rate of decomposition was enhanced in nitrogen. In air, the weight losses slowly decreased, and this suggested that for UP-6, the presence of DOPO pendent groups promoted char residue formation. This residue could have been subjected to oxidation in air, so at the end of the thermal decomposition process, the decomposition residues were fewer in air versus nitrogen.

Figure 3(a,b) shows the TG and DTG curves for phosphorus-modified samples with different substitution degrees (UP-4, UP-6, and UP-10) in nitrogen and air atmospheres, respectively.

Some remarks can be made about the thermal and thermooxidative stability of the phosphorus-modified PSFs in connection with their substitution degree. Samples UP-4 and UP-6 exhibited the same stability in nitrogen up to 410°C, but a slight decrease in the thermal stability was observed when the substitution degree increased from UP-4 to UP-6. When the substitution degree was much higher (UP-10),
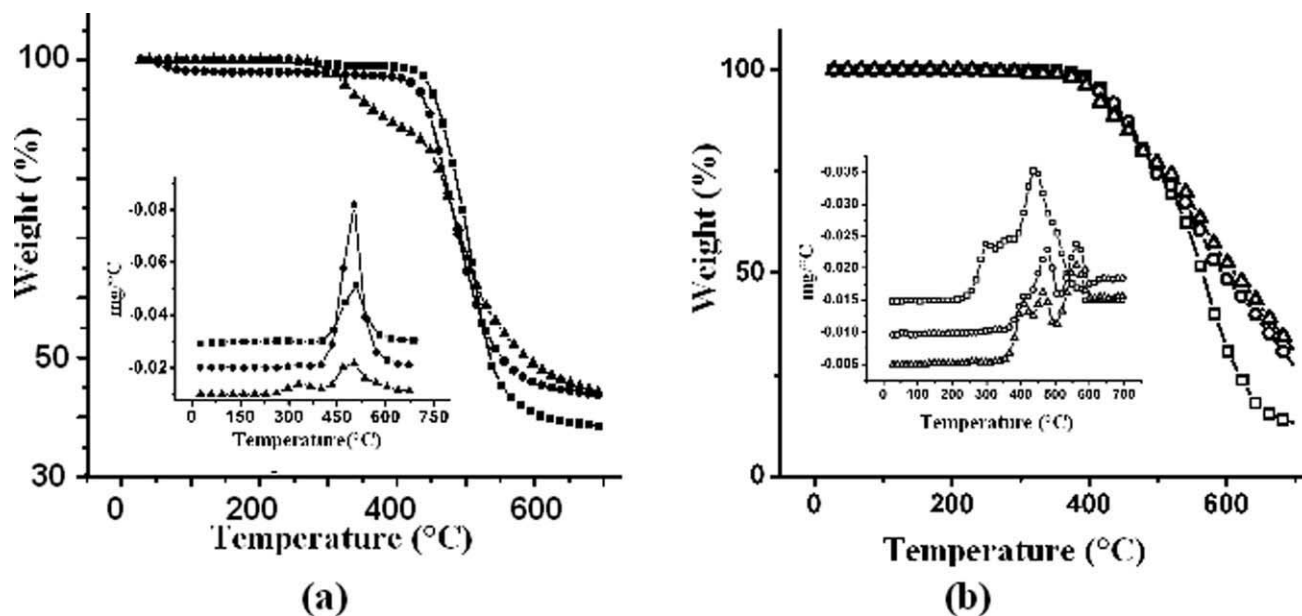
Figure 3 (a) TG and differential weight-loss DTG curves of (■) UP-4, (●) UP-6, and (▲) UP-10 at a heating rate of 10°C/min in nitrogen and (b) TG and differential weight-loss DTG curves of (□) UP-4, (○) UP-6, and (△) UP-10 at a heating rate of 10°C/min in air.

the thermal stability markedly decreased in nitrogen. A relation between the substitution degree and residue percentages was also observed; in nitrogen, the residue increased when the substitution degree increased from 0.62 (UP-4) to 0.72 (UP-6). When the substitution degree increased to 1.3 (UP-10), the residue, instead of being higher, remained close to that of UP-6. This unusual behavior could be related to the possible substitution of the structural unit of chloromethylated

bisphenol (CMPS-10) by two bulky DOPO groups, which affected the heat stability, and could have led to the breaking of some fragments below 300°C.[5] Table II lists the following TG data: the onset temperature of polymer decomposition (T_{Onset}), the thermal degradation peak corresponding to the temperature of decomposition (T_{Peak}), the thermal degradation end-set temperature (T_{Endset}), the mass loss corresponding to each stage, and the weight loss after decomposition.

TABLE II
TG Characteristics of Chloromethylated and Phosphorus-Modified PSFs

Sample	Stage of thermal degradation	Nitrogen atmosphere					Air atmosphere				
		T_{Onset} (°C)	T_{Peak} (°C)	T_{Endset} (°C)	Mass loss (%)	Weight loss after decomposition (%)	T_{Onset} (°C)	T_{Peak} (°C)	T_{Endset} (°C)	Mass loss (%)	Weight loss after decomposition (%)
CMPS-4	I	314	338	368	5.49	41.96	324	344	360	3.73	5.97
	II	453	516	600	52.55		432	564	641	90.3	
UP-4	I	437	511	576	62.08	37.92	399	424	532	31.14	13.34
	II	–	–	–	–		532	567	652	55.52	
CMPS-6	I	306	326	415	10.58	46.76	318	334	349	6.35	5.87
	II	415	500	700	42.66		411	567	588	87.78	
UP-6	I	431	466	564	54.06	45.94	385	404	442	7.77	27.69
	II	–	–	–	–		442	479	492	18.45	
	III	–	–	–	–		527	565	587	21.81	
	IV	–	–	–	–		587	–	–	24.28	
CMPS-10	I	302	330	396	12.16	45.87	316	343	358	8.04	5.46
	II	440	490	599	41.97		398	562	588	86.5	
UP-10	I	297	321	393	11.16	45.36	382	404	441	13.96	31.45
	II	444	488	600	43.48		441	468	485	9.50	
	III	–	–	–	–		532	556	584	20.78	
	IV	–	–	–	–		584	–	–	24.31	
PSF	I	494	517	584	51.23	48.77	486	515	534	27.06	23.46
	II	–	–	–	–		585	–	–	49.48	

For both samples, the most important mass loss was recorded in the last stages of thermal and thermooxidative degradation at a temperature onset over $\cong 400°C$. The degradation process exhibited one, two, or four decomposition maxima. For all samples, the degradation processes were not complete, a residue remaining in each situation.

For the CMPS sample, the TG curves obtained by the traditional TG technique at constant heating rates exhibited two steps in nitrogen and in a air atmosphere. In the first stage, T_{Peak} for this sample was 6–13°C higher in air versus a nitrogen atmosphere (Table II). When analyzing the specific temperature range of the thermal degradation process (T_{Endset} - T_{Onset}) in the first stage, we noticed that the CMPS samples had the highest degradation speed in air versus a nitrogen atmosphere. Very little residue remained after the TG experiment in an air atmosphere; however, approximately 42, 47, or 46% of the weight remained after the experiments in nitrogen. Moreover, approximately 5–12% of the compound decomposed over a temperature range of 300–400°C, whereas under an air atmosphere, only 3–8% of these samples (CMPS-4, CMPS-6, and CMPS-10) were decomposed over the same temperature range.

The thermal degradation of samples UP-4 and UP-6 in nitrogen occurred in one degradation step; only UP-10 exhibited two steps. Thermal degradation in air exhibited an additional degradation stage (one or three steps) in comparison with thermal degradation in nitrogen. In air, the degradation mechanism was more complex. In this case, all chemically modified PSFs showed a DTG peak at a low temperature, which probably mainly corresponded to the loss of some aliphatic groups. After the elimination of these groups, a less stable structure than PSF appeared with a peculiar decomposition pathway as a function of the modified polymer structure and the atmosphere employed in the TG apparatus.

It can be noticed from the results given in Table II that the thermal and thermooxidative stability index (T_{Onset} of stage I) of the polymers decreased with the increase in the ratio of substituted functional groups.

A comparison of the T_{Onset} values for the first degradation stage permitted the establishment of the following series of thermal and thermooxidative stabilities:

$$\text{CMPS-10} < \text{CMPS-6} < \text{CMPS-4}$$
$$\text{and}$$
$$\text{UP-10} < \text{UP-6} < \text{UP-4} < \text{PSF}$$
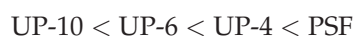
FTIR study of the solid pyrolysis products

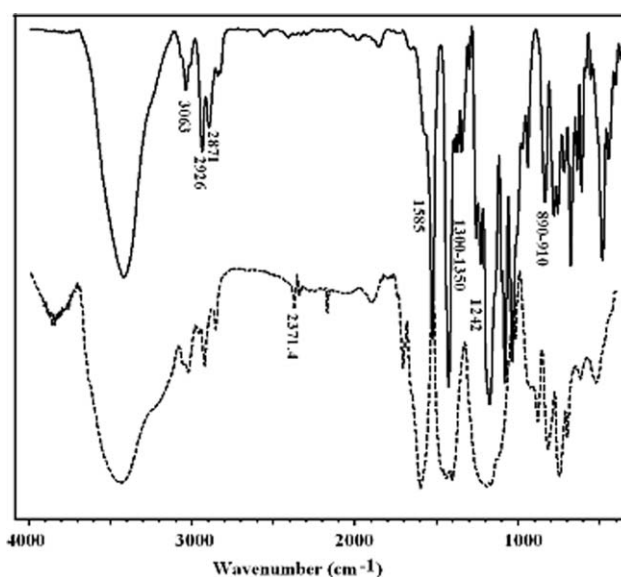To support the results of the TG analysis and to better understand the pyrolysis reactions, we under-

Figure 4 FTIR spectra of (—) phosphorus-modified PSF UP-6 and (···) its decomposition residue in an inert atmosphere at 600°C.

took FTIR studies of solid and volatile decomposition products in an inert atmosphere and in air.

The FTIR spectra of the phosphorus-modified PSF UP-6 and its decomposition residue in an inert atmosphere at 600°C are presented in Figure 4.

The most important absorption bands for UP-6 were those associated with aromatic C—H (3063 cm^{-1}), aliphatic C—H (2926 and 2871 cm^{-1}), the aromatic ring for the DOPO structure (1585 cm^{-1}), the —SO$_2$— vibration (1300–1350 cm^{-1}), the P=O stretching vibration superposed with C—O—C (1242 cm^{-1}), and aliphatic P—O (890–910 cm^{-1}).

The changes observed in the FTIR spectrum after UP-6 decomposition at 600°C in an inert atmosphere (54% weight loss) involved the formation of polyaromatic structures (1897 and 1597 cm^{-1}) and the appearance of carbonyl groups (1704 cm^{-1}). It was especially evident that the organophosphorous P—O—C groups were incorporated into the solid residue (the enlargement of P=O and P—O—Ar peaks at 1250 and 1450 cm^{-1}, respectively, and the reappearance of P—H at 2436 cm^{-1}). It seems that the DOPO groups or different fragments containing it remained mainly in the nonvolatile fraction when the polymer decomposed in an inert atmosphere. A strong absorption could be observed at 3400 cm^{-1}. After pyrolysis, the residue was reached in phosphorus-containing fragments, even in phosphoric acid, which increased its hydrophilic behavior. Consequently, the absorption at 3400 cm^{-1} increased because of —OH stretching resulting from the hydrophilic phosphorus-containing fragments.

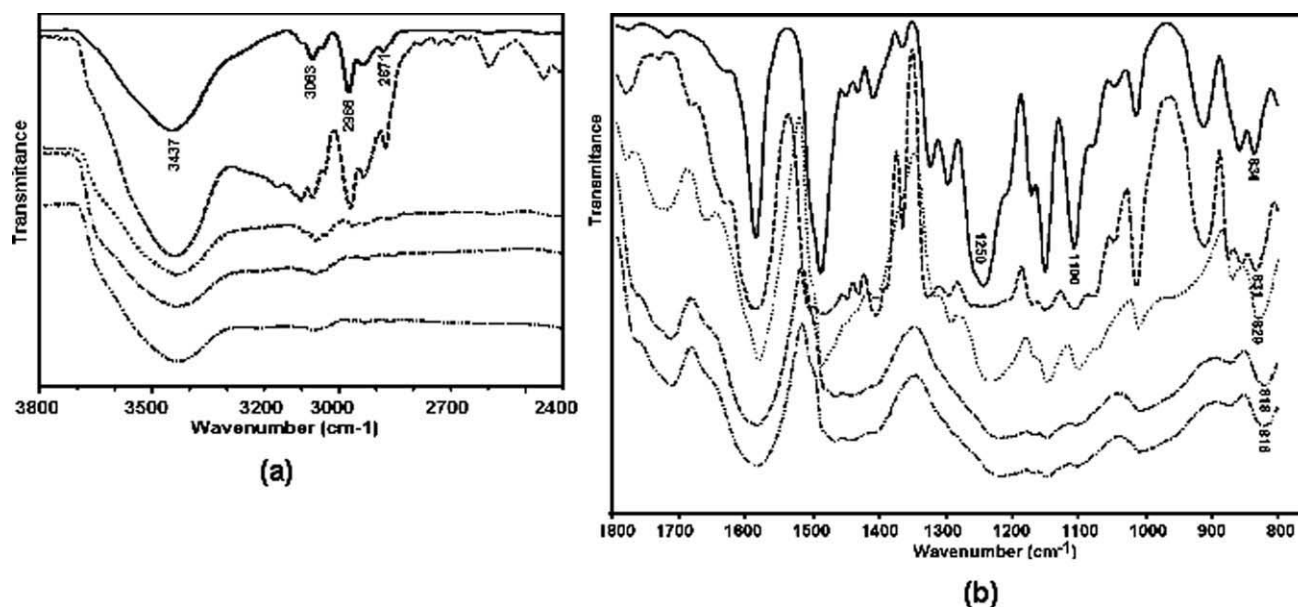When UP-6 decomposed in air, completely modified FTIR spectra were recorded at different heating

Figure 5 FTIR spectra of phosphorus-modified PSF UP-6 and the products of its thermooxidative decomposition (a) in the range of 3800–2400 cm^{-1} and (b) in the range of 1800–800 cm^{-1}: (——) initial UP-6, (—— ——) residue at 300°C, (●●●) residue at 450°C, (——●——) residue at 500°C, and (——●●——) residue at 600°C.

temperatures. Figure 5(a) presents the FTIR spectra in the 2400–3800-cm^{-1} range for UP-6 and the products of its thermooxidative decomposition on heating at 10°/min (300, 450, 500, and 600°C). Heating at 10°C/min to different temperatures produced a decrease in the aliphatic C—H asymmetric and symmetric stretching vibrations between 2966 and 2870 cm^{-1} in the FTIR residue spectra over the 2400–3800-cm^{-1} range. This process was finished at 600°C.

In the 600–1800-cm^{-1} range, the FTIR residue spectra presented the most obvious thermooxidative behavior of the phosphorus-containing PSF [Fig. 5(b)]. Solid pyrolysis residues exhibited absorption bands for the aromatic P—O—C groups incorporated into the residue at 831 cm^{-1} and for the P—aryl and P=O organophosphorous groups at 1010–1250 cm^{-1}. The position of the absorption peak at 831 cm^{-1} was shifted to lower wave numbers when the spectra were recorded for pyrolysis residues at higher temperatures.

Only at 600°C did the FTIR spectra seem to present a carbonaceous structure, yet a slight contribution of the phosphorus-containing polyarylate structures could not be excluded (broad absorption bands were placed between 1100–1200 and 850–900 cm^{-1}).

An analysis of the solid decomposition products in an inert atmosphere and in air showed that phosphorus existed mainly in the condensed phase.

SEM images of the solid pyrolysis residues resulting after heating in air at 600°C for PSF, CMPS-6, and phosphorus-modified PSF (UP-6) are shown in Figure 6. Porous and open structures of the PSF and CMPS char can be seen. The diameters of the holes were very large, and this indicated that the

decomposition of PSF and CMPS released a lot of gaseous products that penetrated the char. The compact char structure (even an ordered one) observed for UP-6 confirmed the increased resistance to heat and oxygen.

By the determination of the phosphorous content in the UP-6 char residue, a value of 2.07 was obtained; this meant that nearly 60% of this element was inserted into the solid residue.

FTIR study of the volatile pyrolysis products

Figure 7(a,b) shows that the release rates of the volatile products were quite different for CMPS-6 and phosphorus-modified PSF UP-6, respectively. For CMPS, the highest quantity of released volatile products was produced between 32 and 42 min when the temperature reached 320 and 420°C, respectively. The intensity of the absorption bands at 3854, 3258, 2357, 1526, 1380, 1186, and 516 cm^{-1} was highest and corresponded to the phenol moiety (3854 and 3258 cm^{-1}), CO_2 (2357 cm^{-1}), carbonyl components (1526 cm^{-1}), SO_2 (1380 and 1186 cm^{-1}), and C—Cl groups (516 cm^{-1}).

For UP-6, only a low quantity of volatile products, consisting especially of phenol, carbon dioxide, and an SO_2 derivative, was released. The main release step was produced after 50 min of heating; afterwards, the release of volatile products decreased. The 937-cm^{-1} band (the P—O—C stretching vibration) could prove the hypothetic presence of volatile phosphorus-containing fractions, but only to a certain extent.
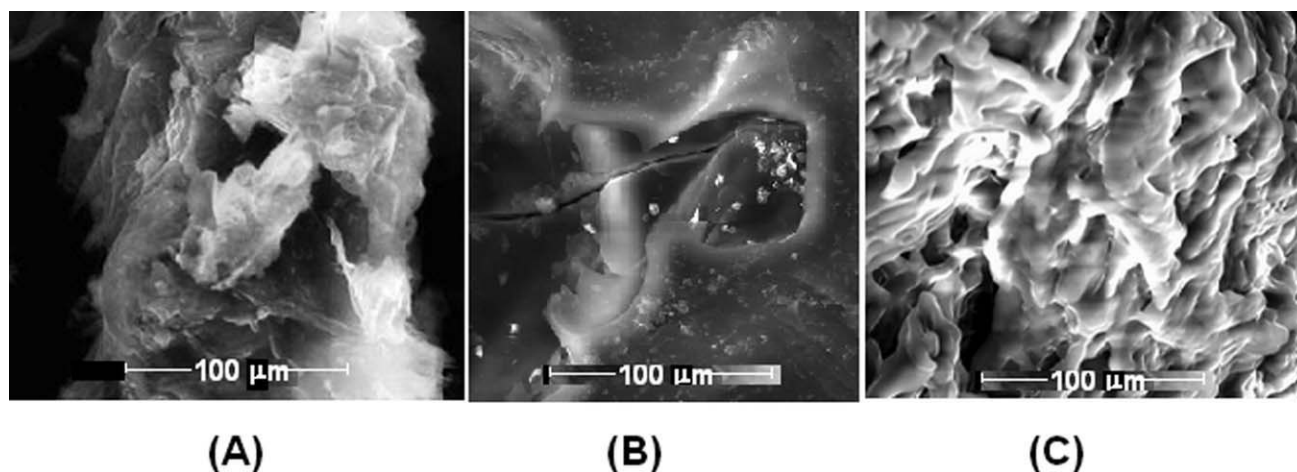
Figure 6 SEM images of the solid pyrolysis residues after heating in air at 600°C for (A) PSF, (B) CMPS-6, and (C) phosphorus-modified PSF UP-6.

To obtain a more precise look inside the composition of the volatile decomposition products in an inert atmosphere, a comparison of the mass spectra of CMPS-6 and UP-6 released from pyrolysis at 300, 450, and 530°C was made (Fig. 8).

The MS spectra recorded for CMPS-6 presented a number of peaks, the occurrence of which could be assigned to the CH_3 fragments bound to an electronegative functional group (15), CH_4 (16), CO_2 (44), SO_2 (64), aromatic structures such as benzene (78), Ar—O, or unsaturated hydrocarbons (107). HCl could not be identified from the MS spectra recorded for CMPS-6. Homolysis of the C—Cl bond took place primarily on account of the low value of its bonding dissociation energy (78.15 kcal/mol). However, the value of the bond dissociation energy between the C—CH_3 atoms of the isopropylidene group was lower (60 kcal/mol), whereas between the C—CH_2Cl atoms,

it was 71 kcal/mol; in the first step of CMPS thermal degradation, Cl and CH_3 radicals were probably present together, and chlorine aliphatic fragments thus resulted. The question is whether the chlorine radical reacted with the different moieties of the polymer chain or CH_2Cl fragments appeared from the breaking of the functional group. Similar observations were made for the thermal degradation of brominated and bromomethylated PSF.[15]

When the CMPS mass spectra were registered at different temperatures, only slight differences related to the abundance of these major peaks could be observed.

When a UP-6 MS spectrum was recorded at 300°C, a small number of peaks could be detected. At this temperature, UP-6 was still thermostable. When MS was recorded at higher temperatures, the occurrence of more numerous peaks confirmed the presence of aromatic structure fragments with higher
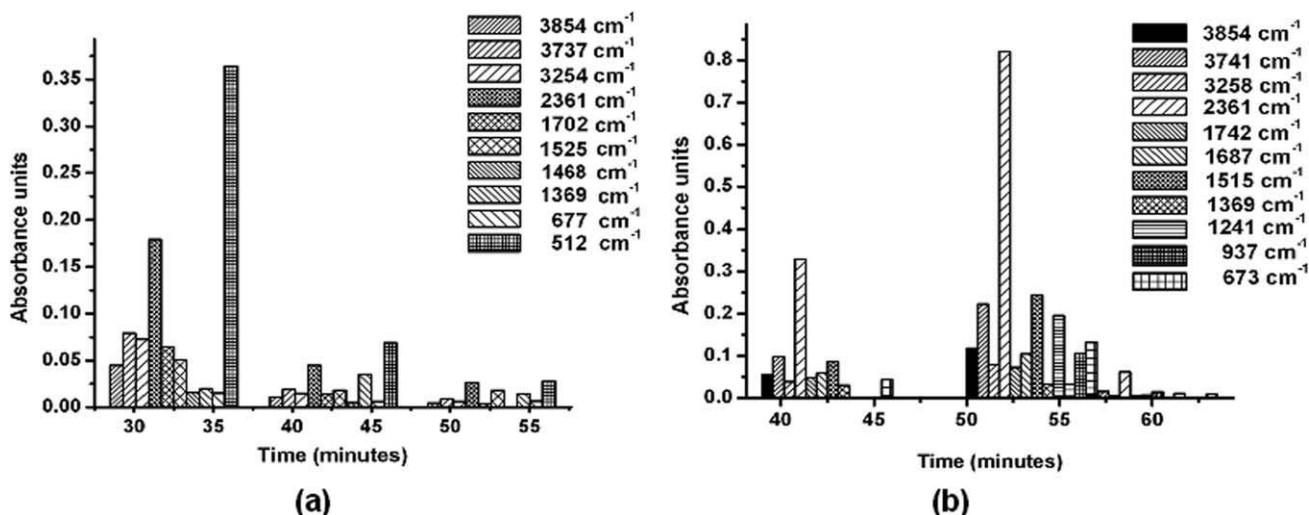

Figure 7 Release rate of volatile pyrolysis products of (a) CMPS-6 and (b) UP-6 as a function of time during thermodegradation at a heating rate of 10°C/min under an inert atmosphere (monitoring via the representative intensity of the absorption bands between 512 and 3854 cm^{-1}).
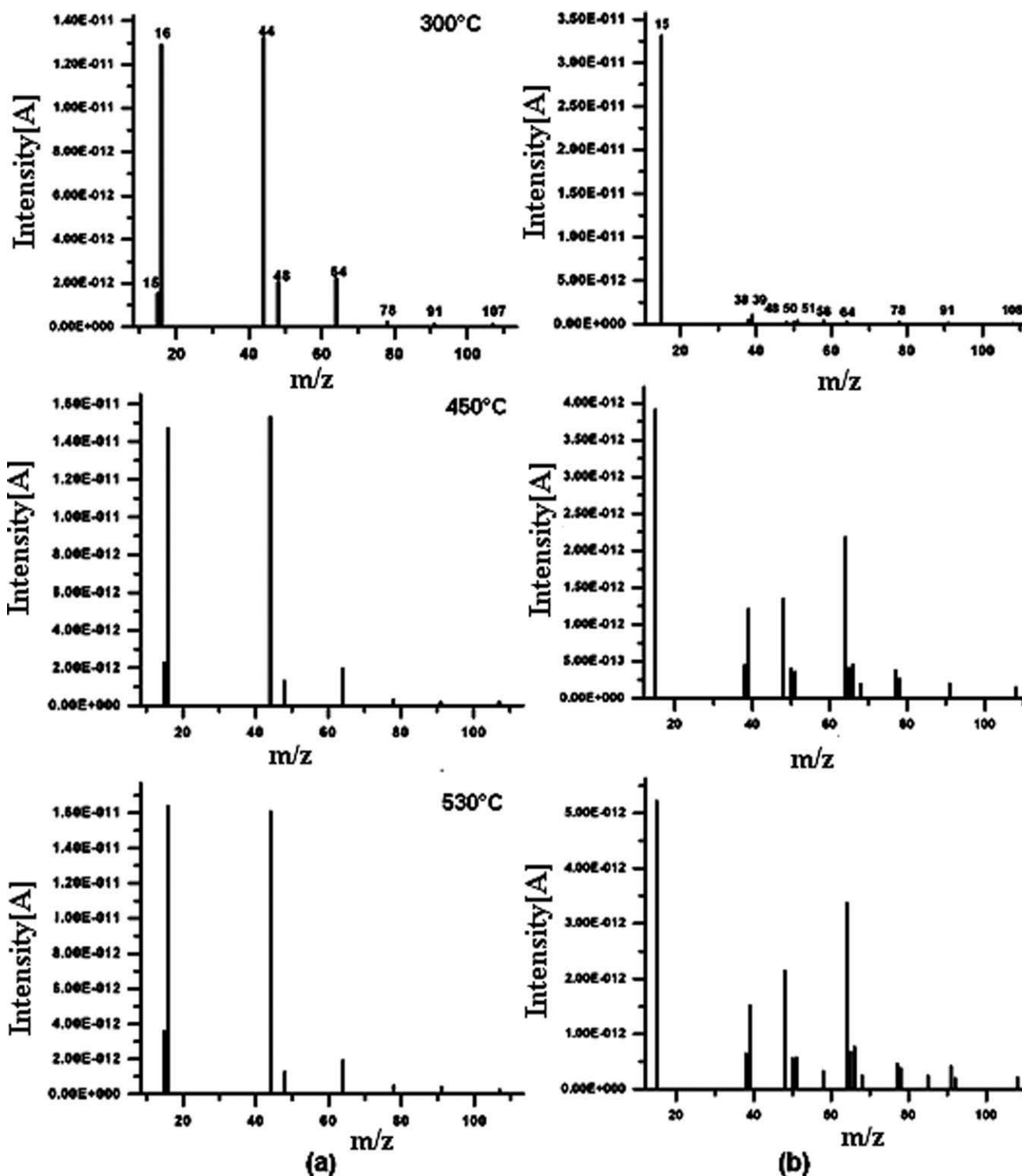
Figure 8   Mass spectra recorded for (a) CMPS and (b) UP-6 at different temperatures.

masses (77, 78, 91, and 108). The peak at 108, evidencing a certain abundance, could be assigned to polyunsaturated cyclic hydrocarbons.[16] Because no more peaks could be found up to a mass of 108, the probability of finding proofs of the presence of phosphorous aromatic fragments in the volatile pyrolysis products was much reduced.

Figure 9(a,b) illustrates the abundances of different mass fragments versus the temperature for CMPS-6 and UP-6, respectively. Quantities of volatile fragments with lower masses, appearing between 400 and 525°C, were enhanced for CMPS; fragments with higher masses also appeared at these temperatures. Similar volatile fragments were
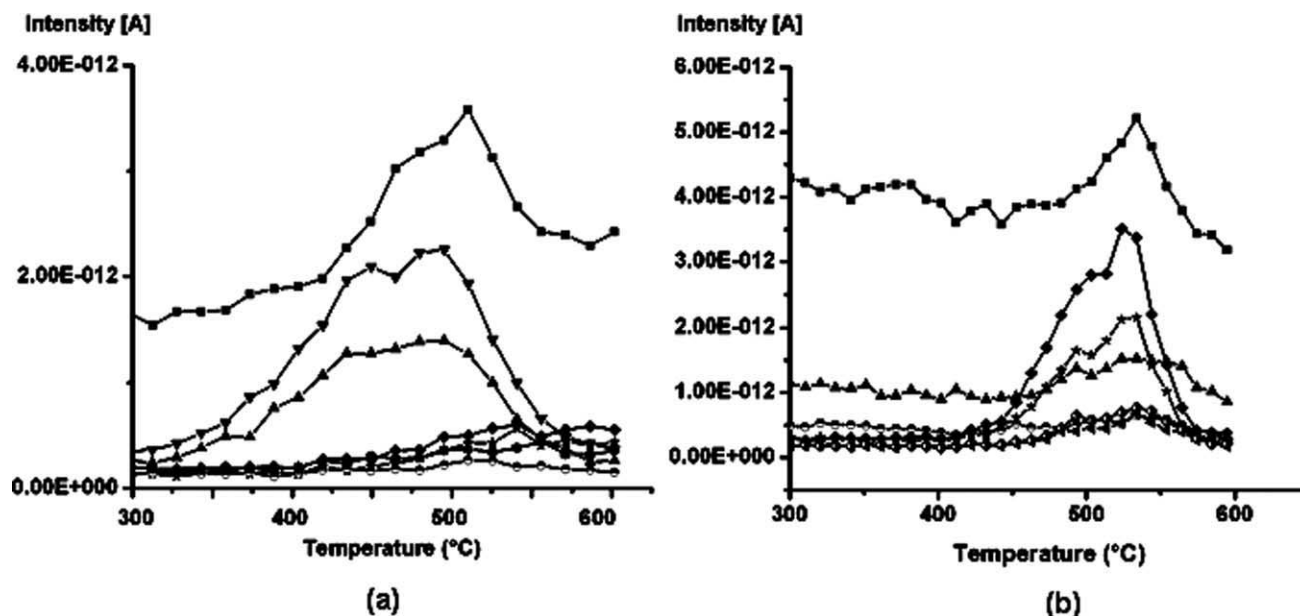
Figure 9 Abundance of different mass fragments versus the temperature for (a) CMPS [mass = (——■——) 15, (——▲——) 48, (——▼——) 64, (——◄——) 77, (——◆——) 78, (——★——) 91, or (——●——) 107] and (b) UP-6 [mass = (——■——) 15, (——○——) 38, (——▲——) 39, (——★——) 48, (——◆——) 64, (——◄——) 66, or (——◇——) 67].

evolved for UP-6 with a lower intensity, their maximum appearance being recorded up to 525°C. It seems that the presence of phosphorus in the UP-6 structure led to a reduced rate of volatile and flammable fragments.

CONCLUSIONS

Chemical modifications of PSFs through chloromethylation and subsequent phosphorous modification essentially changed their thermal behavior. The thermal stability was not so different in nitrogen and air atmospheres up to 410°C, although in nitrogen, a slight decrease was observed when the substitution degree increased. A relation between the substitution degree and residue percentages was observed: in nitrogen, the residue decreased with the substitution degree increasing, but in air, an increase in the residue percentage was observed when the substitution degree was enhanced.

Phosphorus-modified PSFs decomposed in two or four degradation steps as a function of the atmosphere employed. In an inert atmosphere, it seems that the DOPO groups or the different fragments containing them remained mainly in the nonvolatile fraction, but a low quantity of volatiles containing phosphorus was also detected. In air, the DOPO pendent group promoted the formation of a more compact char residue, which could prevent the attack of heat. Oxidation of the unsaturated char residue reduced the quantity of decomposition residues

in comparison with those resulting after pyrolysis in nitrogen.

References

1. Zhang, A.; Li, X.; Nan, C.; Hwang, K.; Lee, M.-H. J Polym Sci Part A: Polym Chem 2003, 4, 22.
2. Avram, E.; Butuc, E.; Luca, C.; Druta, I. J Macromol Sci Pure Appl Chem 1997, 34, 1701.
3. Cozan, V.; Avram, E. Eur Polym J 2003, 39, 107.
4. Filimon, A.; Avram, E.; Dunca, S.; Stoica, I.; Ioan, S. J Appl Polym Sci 2009, 112, 1808.
5. Petreus, O.; Avram, E.; Serbezeanu, D. Polym Eng Sci 2010, 50, 48.
6. Levchik, S. V.; Weil, E. D. J Fire Sci 2008, 26, 243.
7. Hamciuc, C.; Vlad-Bubulac, T.; Petreus, O.; Lisa, G. Eur Polym J 2007, 43, 980.
8. Petreus, O.; Rosescu, L.; Popescu, F.; Bruma, M. Rev Roum Chimie Bucharest 1994, 34, 971.
9. Petreus, O.; Popescu, F.; Cascaval, C. N. Angew Makromol Chem 1994, 214, 29.
10. Petreus, O.; Vlad-Bubulac, T.; Hamciuc, C. Eur Polym J 2005, 41, 2663.
11. Perez, R. M.; Sandler, J. K. W.; Altstadt, V.; Hoffmann, T.; Pospiech, D.; Ciesielski, M.; Döring, M.; Braun, U.; Balabanovich, A. I.; Schartel, B. Polymer 2007, 48, 778.
12. Deng, Y.; Zhao, C.-S.; Wang, Y.-Z. Polym Degrad Stab 2008, 93, 2066.
13. Balabanovich, A. I.; Pospiech, D.; Korwitz, A.; Hausler, L.; Harnisch, C. Polym Degrad Stab 2009, 94, 355.
14. Haslam, J.; Hamilton, J. B.; Squirrell, D. C. M. Analyst 1960, 85, 556.
15. Molnár, G.; Botyay, A.; Pöppl, L.; Korkos, K.; Borossay, J.; Máthé, A.; Török, T. Polym Degrad Stab 2005, 89, 410.
16. McLafferty, F.; Venkataraghavan, R. Mass Spectral Correlations, 2nd ed.; Advances in Chemistry Series 40; American Chemical Society: Washington, DC, 1982; p 64.