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Novel cyclophosphazene monomers and their polymerization behavior

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Chapter 5

THERMAL BEHAVIOR OF THE INORGANIC-ORGANIC POLYMERS

5.1 Abstract

The thermal behavior of the following systems have been investigated by TGA and XPS: the homopolymers of $N_3P_3Cl_4(Me)(CH_2C_6H_4CH=CH_2)$ (STP) and $N_3P_3(NMe_2)_4(Me)(CH_2C_6H_4CH=CH_2)$ (STPN), copolymers of STP with MMA and styrene and copolymers of $N_3P_3Cl_4(iPr)\{C[OC(O)Me]=CH_2\}$ (VAcP) with MMA and styrene. Upon heating under TGA conditions the highest char yield (64 wt%) is found for the homopolymer of STP. The char yields for the copolymers appear to increase with increasing amounts of phosphazene incorporated. The one step weight loss observed for the homopolymer of STP can be mainly ascribed to elimination of HCl. The STP/styrene copolymers decompose in one step, indicating that HCl elimination, ring degradation and depolymerization take place simultaneously. The STP/MMA copolymers show a two step degradation. From XPS scans it follows that complete loss of chlorine takes place in the first step and probably in combination with some depolymerization of MMA units. In the second step phosphazene ring degradation is observed, accompanied with further carbonization of the sample. The VAcP/styrene copolymers start to decompose about 100 °C lower than the STP/MMA copolymers, exhibiting also a two step TGA curve. The first step can be associated with breakdown of polymer chains at the C-C linkage between inorganic monomers. In the second step depolymerization of the styrene sequences, HCl elimination and ring degradation occurs. PP/styrene copolymers also loose weight in a two step process but polymers with the same composition as the VAcP/styrene polymers give lower char yields. All polymers showed an enhanced flame retardancy.

5.2 Introduction

In literature several olefin substituted cyclophosphazenes have been described [1-5]. In most cases their polymerization behavior in free radical polymerization reactions with common organic monomers like styrene and methyl methacrylate has been studied in detail [1-3]. These hybrid inorganic-organic polymers are of interest because their properties can be easily changed by reacting the P-Cl groups with various nucleophiles [6]. In this way it is possible to meet demands necessary for use in a wide variety of applications. Of these properties, their enhanced flame retardancy and high char yields are the most important [1-3]. For polymers $-\text{[CH}_2\text{CH(ON}_3\text{P}_3\text{Cl}_5\text{)]}_n-$ and $-\text{[CH}_2\text{CH(ON}_3\text{P}_2\text{SOPhCl}_3\text{)]}_n-$ it was shown that at relative low temperatures cross-linking occurred between the cyclophosphazene ligand and the hydrocarbon main chain with elimination of HCl [7,8]. At higher temperatures elimination of $(\text{N}_3\text{P}_3\text{Cl}_5)_2\text{O}$ was observed for the polymer $-\text{[CH}_2\text{CH(ON}_3\text{P}_3\text{Cl}_5\text{)]}_n-$ [8]. In general, the processes involved in thermal degradation of phosphazene containing organic copolymers are however still not completely understood.

To gain more insight into the nature of these processes we have investigated by TGA the thermal degradation behavior of various cyclophosphazene containing polymers. The elemental composition at the various stages of the degradation processes was studied with X-ray photoelectron spectroscopy (XPS or ESCA) [9]. We also investigated whether a difference in composition of the remaining char is obtained when the sample is heated in the TGA under a nitrogen sphere or is burned in a flame.

This Chapter reports the results of the combined TGA and XPS studies on the homopolymer of gem-methyl(vinylbenzyl)tetrachlorocyclotriphosphazene (STP) and its fully amino substituted derivative STPN, copolymers of STP with methyl methacrylate (MMA) and styrene [3] and copolymers of gem-isopropyl-2-(α -acetoxyvinyl)tetrachlorocyclotriphosphazene (VAcP) with MMA and styrene [4,5]. Also copolymers derived from PP and styrene are included in this research.

5.3 Experimental

Measurements

Glass transition temperatures were recorded by using a Perkin-Elmer DSC7 unit. The measurements were carried out at a heating rate of 10 °C/min. Thermogravimetric analyses were carried out with a Perkin-Elmer TGA-7 thermogravimetric analyzer at a heating rate of 10

$^{\circ}\text{C}/\text{min}$ in a nitrogen atmosphere. XPS analyses were performed on a X-Probe 300 of Surface Science Instruments, using monochromated $\text{AlK}\alpha$ radiation with an energy of 1486.6 eV. Each sample was measured with an experimental resolution of 1.8 eV and a take-off angle of 45° .

Materials and procedures

The procedure for the synthesis of the polymers discussed here are described in Chapter 4 of this Thesis.

For the XPS study the residue for the homopolymer of STP and STPN was obtained by casting a polymer film on a silicon wafer and heating it to 900°C at a rate of $5^{\circ}\text{C}/\text{min}$ in a furnace under a nitrogen flow. The other samples obtained in TGA experiments were glued by silverpaste on a silicon waver.

5.4 Results and discussion

5.4.1 TGA studies on homopolymers of STP and STPN

The thermal analyses data of the homopolymers of STP and STPN are summarized in Table 5.1. Both polymers show large char yields, which are higher than the weight percentage PN present in the starting materials. The TGA scan of the homopolymer of STP (run no. 6 in Table 4.1) shows an one-step decomposition starting at 410°C and giving a weight loss of 36% (see Figure 5.1, curve a). The remaining black brittle char is stable up to at least 700°C . Although the observed weight loss corresponds with the amount of HCl present in the polymer (see Table 5.1), it is unlikely that this is the only decomposition process which takes place. It is known that degradation of polystyrene occurs mainly along a depolymerization process [10]. For polystyrene decomposition starts at 400°C and no residue remains. Considering the homopolymer of STP as a polystyrene derivative, one can conclude from the observed one-step degradation process that depolymerization and elimination of HCl takes place simultaneously. Loss of HCl results in a cross-linked matrix which will considerably reduce the loss of weight during the depolymerization process.

For STPN the TGA scan shows that immediately upon heating from room temperature the sample starts losing weight slowly. This can be caused by the loss of unreacted STPN and other low molecular weight material which are probably still present in the polymer as it was not further purified when formed. At 440°C a sharp decrease in weight is observed until about 40 wt% of the starting material remains. This black brittle residue is stable to at least 900°C .

Following the same reasoning as above, it can be expected that the thermal degradation of the homopolymer of STPN proceeds via the same processes as that of STP. However, instead of cross-linking due to HCl formation now elimination of HNMe₂ from the sample takes place.

Table 5.1 Composition and thermal analyses data for the homopolymers of STP and STPN

run no.	PN in copolymer (wt%)	HCl (wt%)	HNMe ₂ (wt%)	T _{onset} (°C)	wt% loss 1 st step	T _{d,50%} (°C)	char ^a (wt%)	T _g (°C)
STP	33.0	35.7	-	411	36.3 ^b	485	63.7	113
STPN	30.4	-	40.7	440	60.2 ^b	460	42.1	
^c	-	-	-	400	100 ^b	415	0	103

^a At 700 °C; ^b weight loss occurs in one step; ^c polystyrene

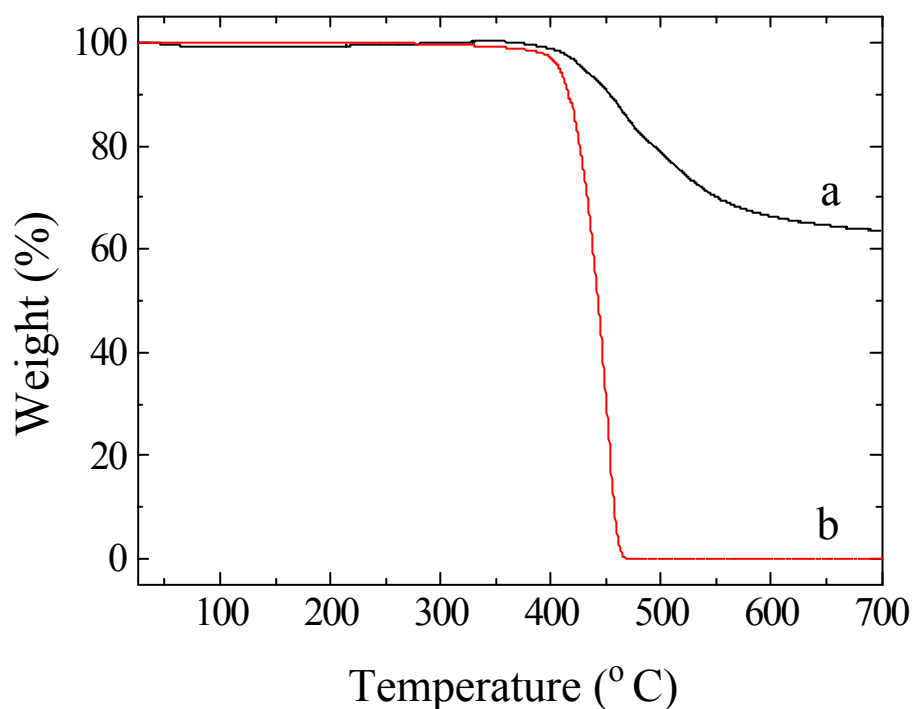


Figure 5.1 TGA scan of STP homopolymer (a) and polystyrene (b)

5.4.2 XPS studies on homopolymers of STP and STPN

The results of these XPS studies are shown in Table 5.2 and Figures 5.2 and 5.3. For a quantitative discussion XPS scans of the starting materials were taken and the calculated atom percentages compared with the experimentally obtained values. As may be seen from Table 5.2 these values are in excellent agreement with each other for the homopolymer of STP. For the polymer formed by STPN the calculated values differ slightly from the experimental found atom percentages probably as a result of impurities in the material.

Table 5.2 Atom% of STP and STPN homopolymers and the residues after heating to 900 °C. Calculated atom% in parentheses

	P	Cl	C	N
homo-STP	16 (15)	20 (20)	51 (50)	13 (15)
residue	19	0	75	6
homo-STPN	8 (11)	-	72 (64)	20 (25)
residue	16	-	78	6

For the homopolymer of STP the composition changes upon heating to 900 °C into a more carbon containing material. Except for the total loss of chlorine from the substrate also about half of the initial amount of nitrogen atoms is lost, resulting in a phosphorus-nitrogen ratio of 3. The ratio of phosphorus to carbon is in the homopolymer of STP about 1 to 3, while in the residue a slightly higher ratio of approximately 1 to 4 is found. From the combined TGA and XPS results it can be concluded that the one-step weight loss observed in the TGA experiment for the homopolymer of STP (Fig. 5.1, curve a) proceeds mainly via elimination of HCl and apparently via degradation of the cyclotriphosphazene ring. Both processes leading to a highly cross-linked material and thus to a high char yield.

If the thermal degradation behavior of the homopolymer of STPN resembles that of the STP homopolymer, the remaining residue of the STPN sample should have the same elemental composition as that found for the STP residue. And indeed this is exactly what is found for both materials.

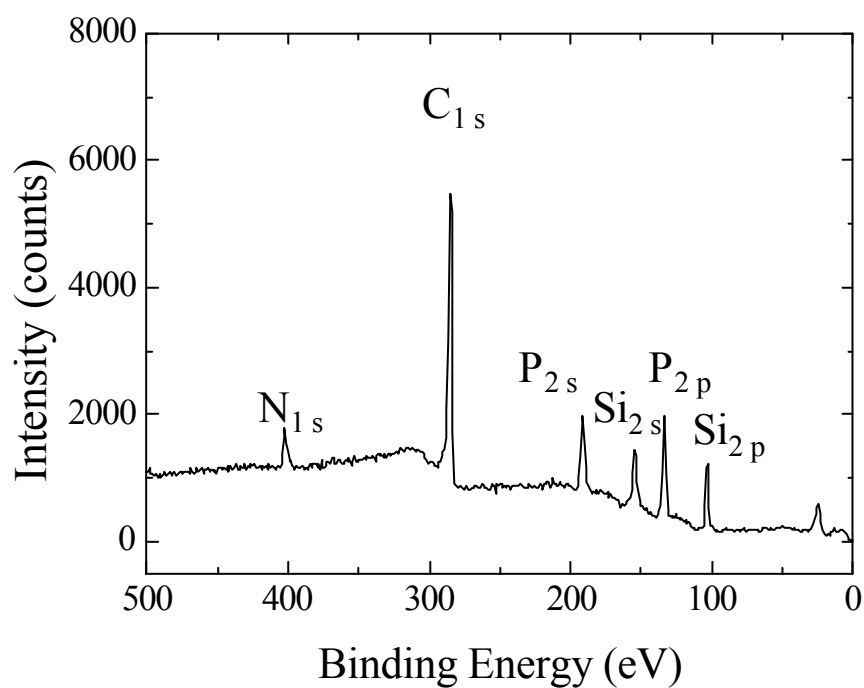
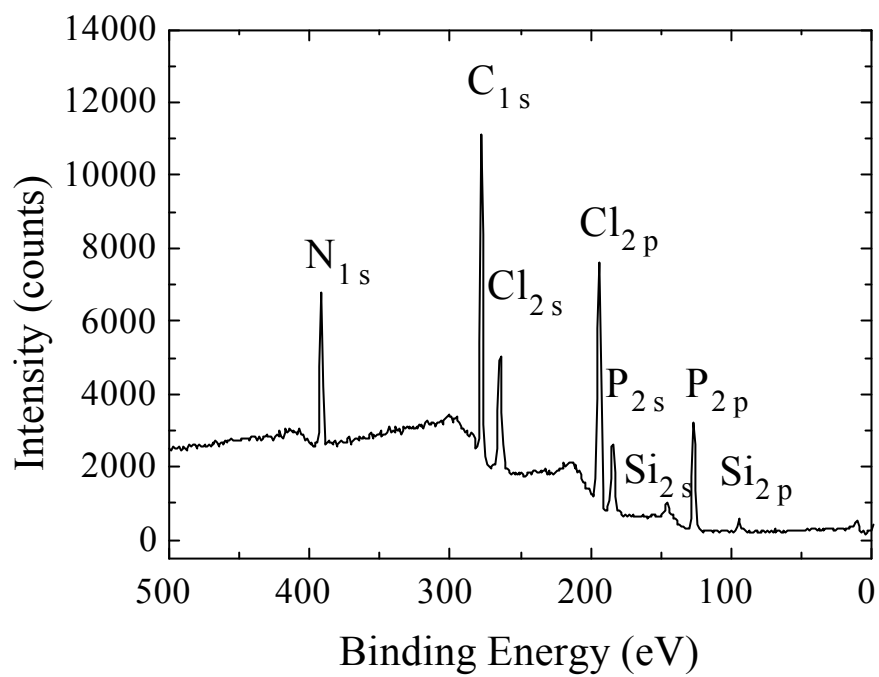


Figure 5.2 XPS spectra of the STP homopolymer (top) and residue after heating to 900 °C (bottom)

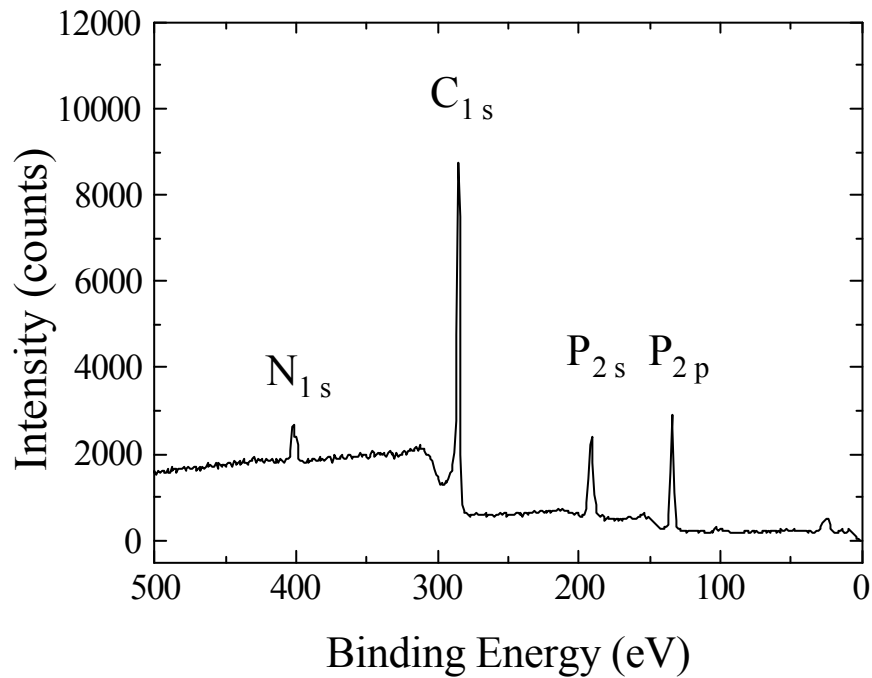
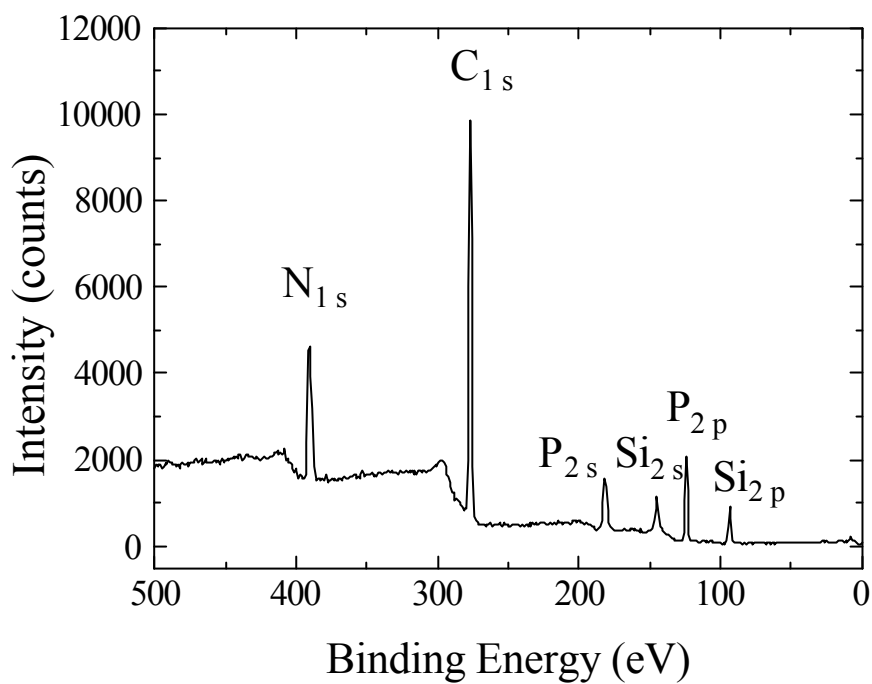


Figure 5.3 XPS spectra of the STPN homopolymer (top) and residue after heating to 900 °C (bottom)

5.4.3 TGA studies on copolymers derived from STP

Table 5.3 lists the obtained thermal analyses data. The above proposed thermal degradation mechanism is supported by the fact that the TGA scans of the copolymers of STP and styrene (run no. 7 and 8 in Table 4.1) also show a weight loss in one step, which takes place in the same temperature range as is observed for polystyrene. It is noteworthy that the STP/styrene copolymer of run no. 8 retains 50% of its original weight at 700 °C (Figure 5.4, curve a). This demonstrates the efficiency of the cross-linking process in the formation of a char as the homopolymer of STP only gives a slightly higher char yield of 64 wt%.

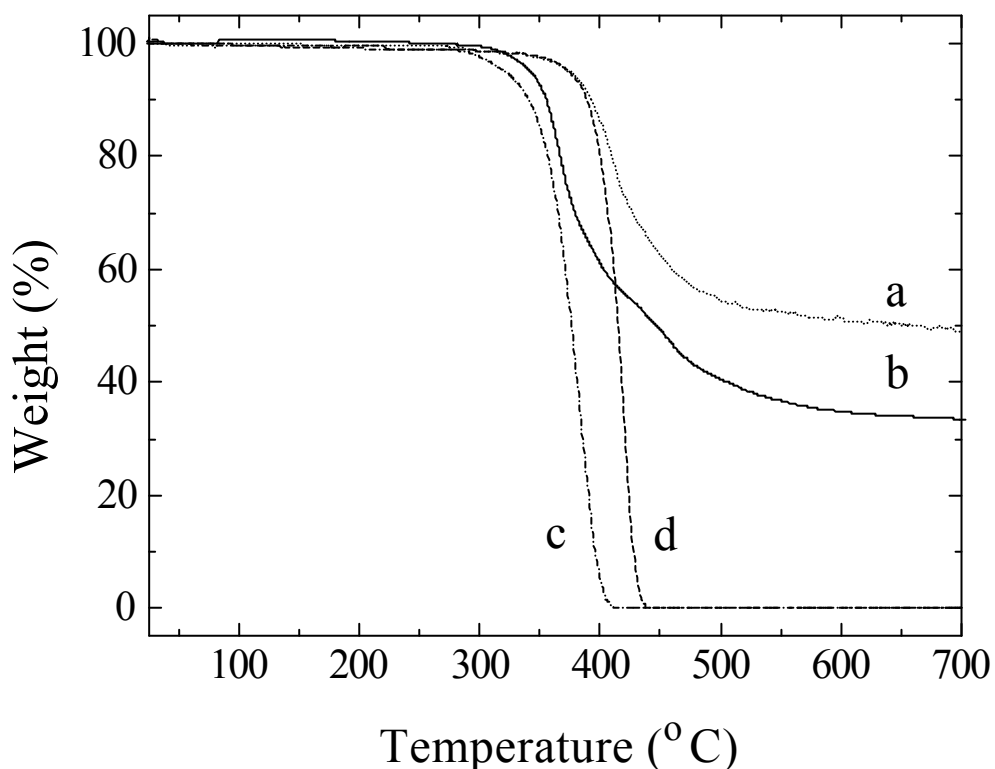


Figure 5.4 TGA curves of the STP/styrene copolymer of run no. 8 (a), STP/MMA copolymer of run no. 10 (b), PMMA (c) and polystyrene (d)

In contrast to the styrene copolymers the copolymers derived from STP and MMA decompose by a two-step process (Figure 5.4, curve b) [9]. The thermal degradation starts at 350-360 °C, which is comparable with the decomposition temperature of PMMA. From this observation it is likely that the first decomposition step of STP/MMA copolymers can be associated with depolymerization of MMA sequences in the copolymer. It also explains why

degradation starts about 30 °C lower than is observed for the styrene copolymers. The high char yield for STP/MMA copolymers points to a cross-linking mechanism comparable with that in STP/styrene copolymers.

Table 5.3 Composition and thermal analyses data for copolymers derived from STP

run no. ^a	STP (mol%)	STP (wt%)	PN (wt%)	HCl (wt%)	T _{onset} (°C)	wt% loss 1 st step ^d	T _{d,50%} ^b (°C)	char ^c (wt%)	T _g (°C)
7	10	30	10	11	393	78 ^d	423	22	105
8	34	67	22	24	383	50 ^d	416	50	109
9 ^e	8	26	9	9	360	31	418	23	124
10 ^e	14	40	13	14	346	41	387	33	123
f	-	-	-	-	400	100 ^d	415	0	103
g	-	-	-	-	349	100 ^d	372	0	124

^a Run no. 7 and 8 with styrene as comonomer and 9-10 with MMA; ^b temperature at which 50% of the total weight loss is observed; ^c at 700 °C; ^d weight loss occurs in one step; ^e ref. 9; ^f polystyrene; ^g PMMA

5.4.4 XPS studies on the STP/MMA copolymer

Because TGA studies showed analogous thermal degradation processes for the homopolymer of STP and STP/styrene copolymers, these copolymers were not further investigated by XPS.

For the copolymer of STP with MMA (run no. 10), which shows a two stage process in TGA, it can be seen that after the first weight loss step no chlorine atoms are detected at 197 and 268 eV in the sample (Table 5.4, Figure 5.5). The resulting char formation is also reflected in the appearance of the material. Because after the first step the material looked visually the same as the residue at 700 °C. The ratio of phosphorus (131 and 189 eV) to nitrogen (400 eV) is not changed, indicating that no ring degradation has occurred at this point of the decomposition. However, the total weight loss in the first step is 41 wt% and only 14 wt% HCl is present in the polymer (Table 5.3). This means that probably also some depolymerization of MMA sequences occurs. After the second step the ratio of phosphorus to nitrogen is raised to 3.5, which is almost the same as observed for the char of the homopolymer of STP. Therefore the main process in the second step seems to involve degradation of the phosphazene ring. A remarkable observation is that the amount of oxygen (529 eV) in the polymer is almost

unchanged during all these stages. As oxygen is incorporated in the side group of the MMA monomer unit it seems that the thermal decomposition does not involve cleavage and subsequent elimination of the methacrylate ligand in carbon dioxide and methane.

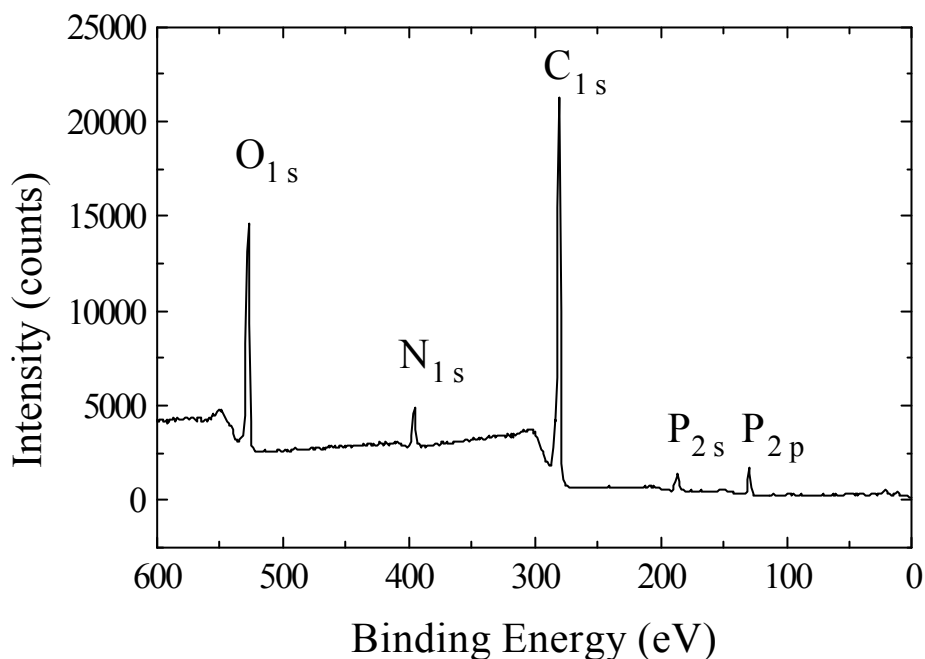


Figure 5.5 XPS spectra of the STP/MMA copolymer (run no. 10) after the first step of weight loss

Table 5.4 Atom% of the copolymers derived from STP and their residues. Calculated atom% in parentheses

run no.		P	Cl	C	N	O
10	STP/MMA	5 (5)	5 (6)	66 (65)	4(5)	20 (19)
	residue after 1 st phase	4	0	73	4	19
	residue after 2 nd phase	7	0	76	2	15
	residue (flame)	5	0	77	2	16

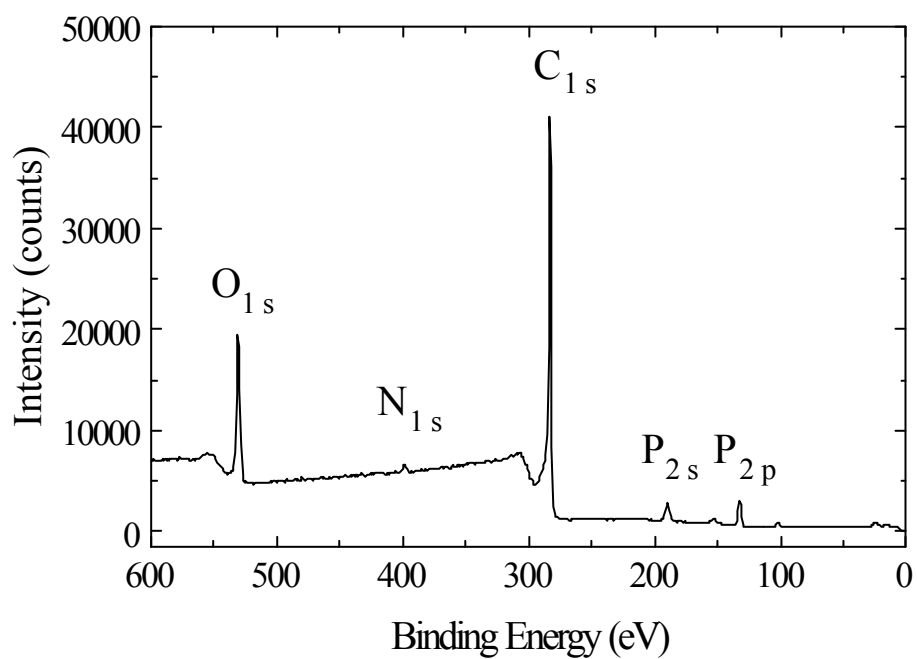
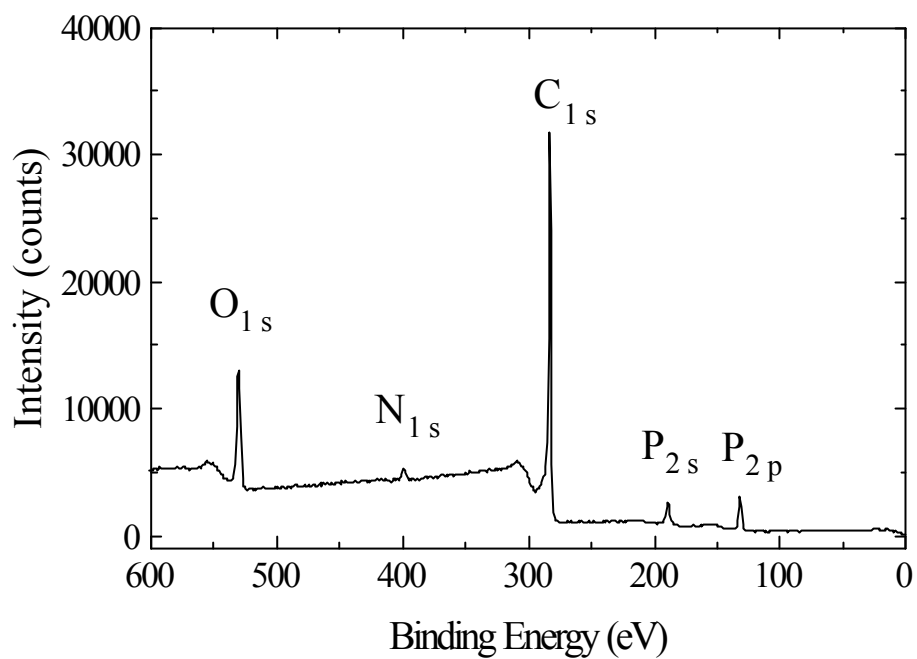


Figure 5.6 XPS spectra of the STP/MMA copolymer (run no. 10) after heating under TGA conditions to 700 °C (top) and after heating in a flame (bottom)

Another remarkable result is the fact that the residue obtained in the TGA under nitrogen atmosphere has the same elemental atom% composition as the polymer sample which was held in a Bunsen burner flame (see Figure 5.6). This suggests that the processes responsible for decomposition are not affected by the presence of oxygen and that any oxidation process that occurs during burning in the flame is efficiently stopped. Probably the phosphorus, nitrogen and/or chlorine atoms play an important role in this. Additives containing these elements are well-known and frequently used to increase the flame retardant properties of organic polymers [11-13].

5.4.5 Polymers of VAcP

The thermal analyses data of the synthesized copolymers of the vinyl acetate derivative, VAcP, with styrene and MMA are summarized in Table 5.5. These polymers were obtained from high conversion radical polymerizations and their compositions are summarized in Tables 4.3 and 4.5 of Chapter 4.

Table 5.5 Thermal analyses data for copolymers of VAcP

run ^a no.	VAcP in copolymer (wt%)	PN	HCl	T _{onset} (°C)	wt% loss 1 st step	T _{d,50%} (°C)	char yield ^b (wt%)	T _g (°C)
1	1.2	0.4	0.4	363	100 ^c	387	0	118
2	4.5	1.5	1.6	344	100 ^c	383	0	126
3	4.9	1.6	1.8	327	100 ^c	378	0	127
13	9	3	3	259	4	412	3	109
17	16	6	6	256	6	404	7	113
19	20	7	7	264	7	400	10	117
22	27	9	10	262	8	400	14	121
23	31	10	11	259	10	393	16	123
24	45	15	16	258	14	382	23	130
^d	-	-	-	400	100 ^c	415	0	103
^e	-	-	-	349	100 ^c	372	0	124

^a Run no. 1 and 2 with MMA as comonomer and 13-24 with styrene; ^b at 700 °C;

^c weight loss occurs in one step; ^d polystyrene; ^e PMMA

The copolymers derived from VAcP and styrene at high conversion show a distinct relation between their T_g values and degree of phosphazene monomer content. As can be seen in Table 5.5, the T_g of the VAcP/styrene copolymers increases when larger amounts of phosphazene are incorporated in the polymer. Probably the introduction of the bulky phosphazene ring and acetoxy groups to the organic backbone of the polymer decreases the flexibility of the main chain which is reflected in a higher T_g . Although the vinyl acetate derivative does not undergo radical homopolymerization under the conditions employed, it is possible to calculate the T_g for the hypothetical homopolymer of VAcP. For that purpose, the well-known Fox equation has been rewritten into a linear form

$$1/T_g = (1/T_{g,VAcP} - 1/T_{g,St}) \times w_{VAcP} + 1/T_{g,St}$$

where T_g is the glass transition temperature (K) of the copolymer, $T_{g,VAcP}$ is the glass transition temperature of the hypothetical homopolymer of VAcP and w_{VAcP} is the weight fraction of the vinyl acetate derivative in the copolymers [14].

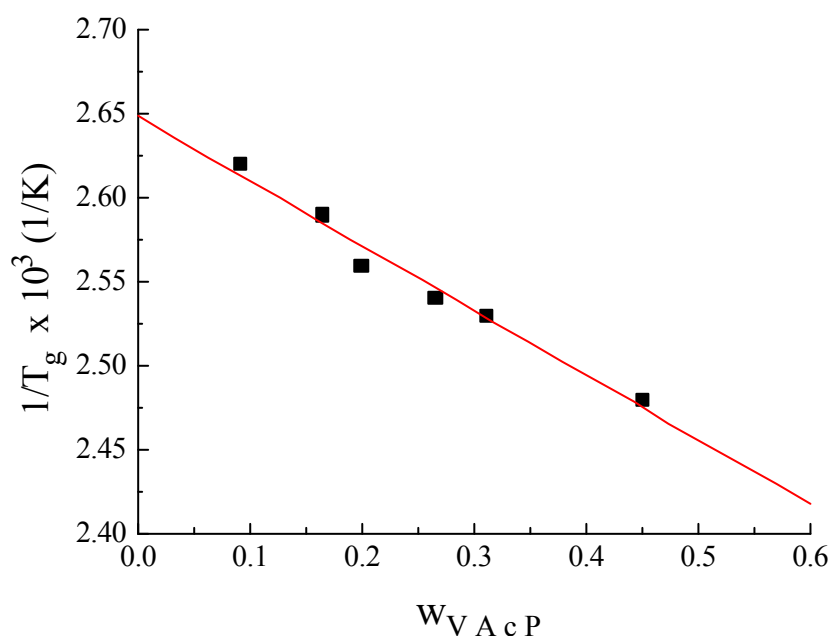


Figure 5.7 Glass transition temperatures T_g of VAcP/styrene copolymers vs weight fraction of VAcP according to the Fox equation

By plotting $1/T_g$ against w_{VAcP} , the data can be fitted satisfactorily by a straight line (correlation coefficient equal to 0.989) (see Figure 5.7). From the slope a $T_{g,VAcP}$ value of 441 K is calculated. Compared with the T_g of 305 K for pure poly(vinyl acetate), the glass transition temperature of the hypothetical homopolymer of VAcP is raised by 136 K due to the substitution of the α -hydrogen atom at the carbon main chain by the phosphazene substituent [15]. This clearly demonstrates the large steric influence of the inorganic component when no spacer is used. On extrapolation to $w_{VAcP} = 0$ the value of $T_{g,St}$ should coincide with that of pure polystyrene. The obtained value of 377 K is in excellent agreement with the experimental value of 373 K [15].

5.4.6 TGA studies on polymers derived from VAcP

The results of the TGA studies on the copolymers of VAcP are also listed in Table 5.5. As can be expected the amounts of the vinyl acetate derivative in the MMA copolymers are too small to have a marked influence on the thermal behavior (Figure 5.8, curve a). Therefore these polymers were not investigated further.

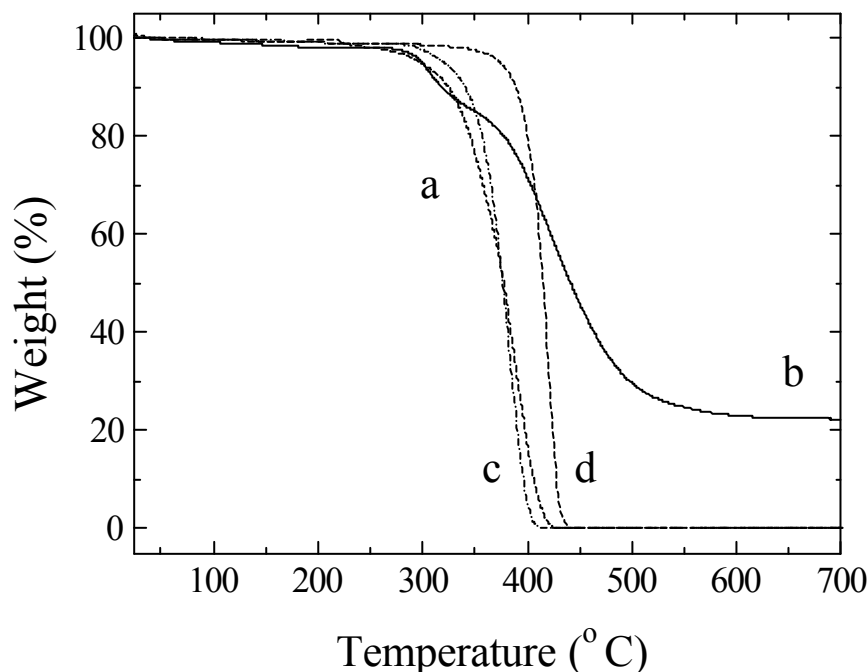


Figure 5.8 TGA scans of the VAcP/MMA copolymer (run no. 3) (a), VAcP/styrene copolymer (run no. 24) (b), PMMA (c) and polystyrene (d)

The incorporation of the phosphazene monomer has a dramatic effect on the thermal stability of the styrene copolymers. With VAcP incorporated decomposition starts at a much lower temperature than is observed for pure polystyrene and occurs in two steps (see Figure 5.8, curve b). Increasing the amount of phosphazene monomer units in the copolymers does not influence the temperature at which the weight loss starts, but the observed $T_{d,50\%}$ (temperature at which 50% of the total weight loss is observed) decreases. This means that the rate of decomposition increases with increasing content of VAcP in the polymer. Higher char yields are observed with increasing amounts of VAcP incorporated. As can be seen the weight loss in the first step increases with increasing phosphazene content, while the weight loss in the second step is decreasing with increasing amounts of VAcP. However, the char formation process for copolymers with VAcP is less efficient than observed for copolymers of STP. To get a residue of 23 wt%, a copolymer with 45 wt% of the vinyl acetate derivative VAcP has to be used instead of a copolymer with 26 (MMA as comonomer) or 30 wt% (comonomer styrene) in the case of the styrene derivative STP.

To explain these phenomena one has to consider that thermal degradation of vinyl polymers proceeds mostly by an unzipping reaction, which is essentially the reverse of the polymerization reaction [10]. Depolymerization starts at the ceiling temperature and this temperature is lower for 1,1-disubstituted monomers than for monosubstituted monomers. As the phosphazene monomer has larger substituents on the double bond than styrene and MMA depolymerization starts at a lower temperature than is observed for pure polystyrene and poly(methyl methacrylate). Because VAcP initiates the formation of radical chain ends and the VAcP/styrene copolymers contain mostly styrene units (see Table 4.5), the weight loss in the first stage will be mostly the result of loss of styrene. This mechanism also explains why with increasing amounts of VAcP units incorporated the weight loss in the first step increases as well as the speed of the process (decreasing $T_{d,50\%}$). In copolymers with high amounts of VAcP incorporated more radical chain fragments are formed and consequently more monomer is liberated in the same time interval when compared with copolymers with a lower VAcP content.

The formation of char is indicative for a cross-linking mechanism during the degradation process. From earlier observations [7,8] it is probably that during the second stage of the decomposition process cross-linking of the polymer takes place accompanied with the elimination of HCl and further depolymerization of the styrene sequences in the copolymer. This also explains why in the second step char yields increase with higher phosphazene contents, thus higher Cl contents.

5.4.7 XPS studies on polymers derived from VAcP

The XPS results for the VAcP/styrene copolymer of run no. 24 (see Figure 5.9) shows a totally different thermal degradation process than is observed in the case of the STP/MMA copolymer (Figure 5.5). In this case the chlorine peaks are still present in the sample after the first weight loss step (Table 5.6). Furthermore the total elemental composition is not changed significantly and the sample looked visually like a clear light-brown polymer film. This clearly indicates that no char formation, i.e. cross-linking by HCl elimination and/or phosphazene ring degradation has occurred and that indeed the first step can be mainly assigned to depolymerization induced by the inorganic monomer units in the copolymer. After the second step the composition of the sample alters drastically. No chlorine atoms are observed anymore and the phosphorus-nitrogen ratio is as in the other samples raised to 3.5. Surprisingly, the relative amount of oxygen atoms (529 eV) in the char increases considerably.

Table 5.6 Atom% of the polymers derived from VAcP and their residues. Calculated atom% in parentheses

run no.		P	Cl	C	N	O
24	VAcP/styrene	5 (5)	7 (7)	78 (79)	5 (5)	5 (4)
	residue after 1 st phase	5	5	82	4	4
	residue after 2 nd phase	7	0	73	2	18

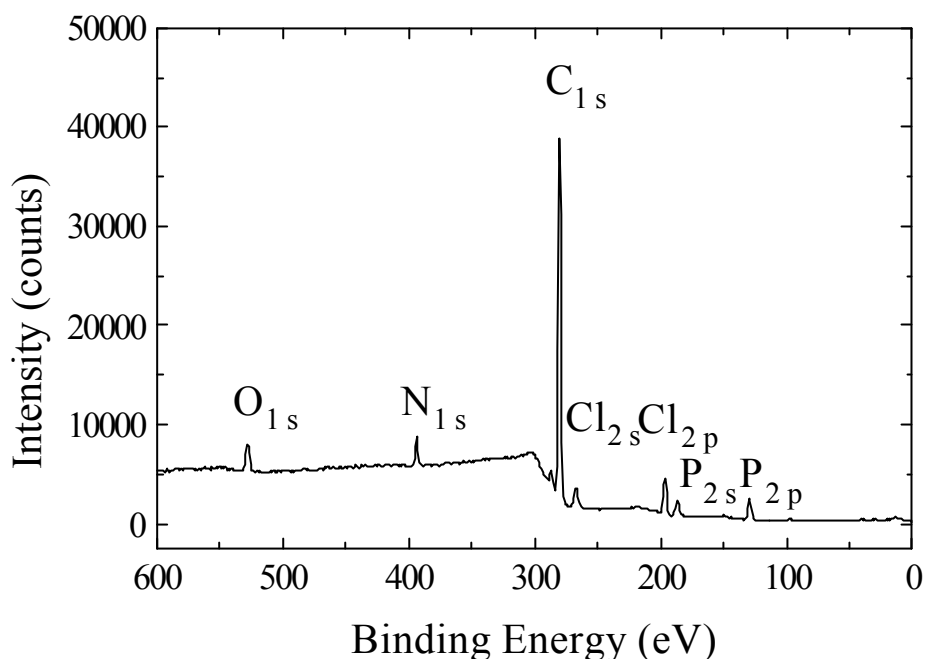


Figure 5.9 XPS spectrum of the VAcP/styrene copolymer of run no. 24 after the first step of weight loss

These results can explain why the copolymers derived from STP and styrene or MMA show higher char yields with the same amount of chlorophosphazene present compared with those obtained from VAcP with styrene. In the case of STP, the weight loss resulting from depolymerization will be limited to a large extent by the simultaneously cross-linking arising from HCl elimination. For copolymers of VAcP and styrene a less efficient process seems to take place. Here depolymerization is probably induced by the cleavage of weak spots in the polymer due to incorporation of VAcP monomer units leading to subsequent elimination of monomer at relative low temperature. This will result in the breakdown of the polymer chains into smaller fragments. Consequently, the cross-linking process by the elimination of HCl and the phosphazene ring degradation at a higher temperature will be less efficient since more and smaller chains have to be tied together to form a char.

5.4.8 TGA studies on polymers derived from PP

The thermal decomposition behavior of the polymers derived from PP and styrene or MMA were only investigated by TGA. Results are summarized in Table 5.7. As is observed for the VAcP/MMA copolymers, the PP/MMA copolymer (run no. 4) does not contain

enough phosphazene monomer to influence the thermal behavior significantly, except that a two steps process is followed.

Table 5.7 Thermal analyses data for copolymers of PP

run ^a no.	PP in copolymer (wt%)	PN	HCl	T _{onset} (°C)	wt% loss 1 st step	T _{d,50%} (°C)	char yield ^b (wt%)	T _g (°C)
1	14	5	6	429	100 ^c	450	1	98
2	35	13	14	308	13	435	8	122
4	1.1	0.4	0.4	280	10	380	0	124
^c	-	-	-	427	100 ^c	443	0	103
^d	-	-	-	349	100 ^c	372	0	124

^a Run no. 1 and 2 with styrene as comonomer and 4 with MMA; ^b at 700 °C;

^c polystyrene; ^d PMMA; ^e weight loss occurs in one step

The PP copolymer of run no. 1 loses slowly about 10 wt% upon heating up to 430 °C after which the polymer mass is lost in one step. The TGA scan of the copolymer of run no. 2 shows a two step weight loss process (Fig. 5.10, curve a) but it is less pronounced compared with the scans of the STP/MMA (Fig. 5.4, curve b) and VAcP/styrene (Fig. 5.8, curve b) copolymers. Compared with VAcP/styrene copolymers, which have about the same copolymer composition as those of run no. 1 and 2 (see Table 5.5, run no. 17 and 24), it is noted that the char yield for the PP copolymers is much lower. Apparently the main decomposition seems to involve depolymerization without extensive cross-linking through HCl elimination.

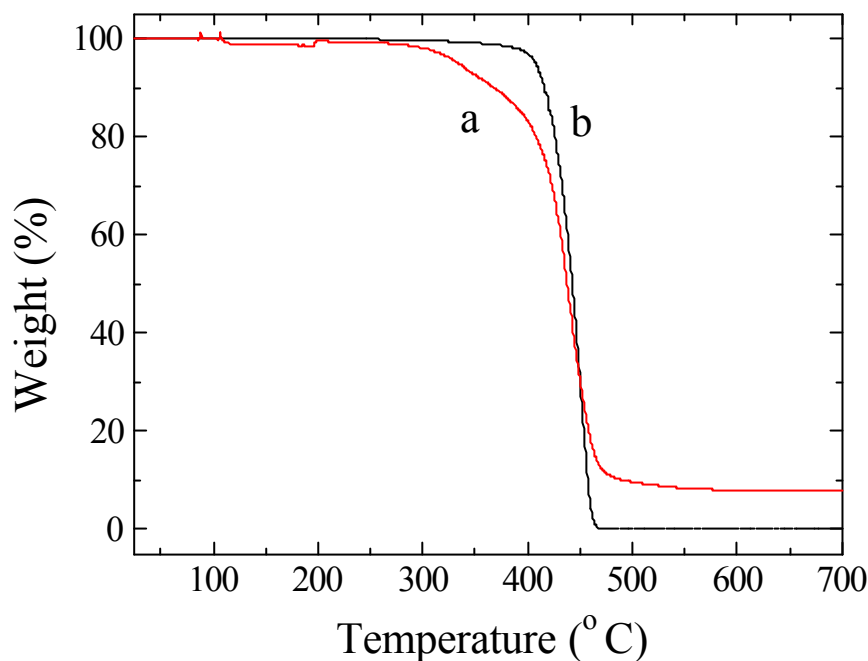


Figure 5.10 TGA scans of the PP/styrene copolymer of run no. 2 (a) and polystyrene (b)

5.4.9 Flame retardancy of the phosphazene containing polymers

The observed char yields also reflect the flame retardant behavior of the phosphazene copolymers. All the synthesized polymers were subjected to the crude flame test. Upon holding the samples in the blue flame of a Bunsen burner they did not liquefy (except for the PP/styrene sample of run no. 1). Inflammation of gaseous decomposition products was observed but when the samples were placed outside the flame they self-extinguish immediately or after a few seconds depending on the amount of phosphazene incorporated. After heating a black brittle material remained, which could be heated until glowing without any visible changes. Only the VAcP/MMA copolymer of run no. 1 and the PP/MMA copolymer of run no. 4 burn outside the flame. These copolymers have only 0.3 mol% of phosphazene incorporated which seems to be below the threshold value to render a polymer flame retardant. In this respect the copolymer of styrene with only 1.4 mol% of VAcP incorporated (run no. 12) is of particular interest. The physical properties resemble those of polystyrene and apparently this small amount of phosphazene monomer is sufficient to provide the polymer with flame retardant properties.

5.5 References

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