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Commercial Fire-retarded PET Formulations – Relationship Between Thermal Degradation Behaviour and Fire-retardant Action

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ABSTRACT

Many types of fire-retardants are used in poly(ethylene terephthalate), PET, formulations, and two commercial fire retardants, Ukanol® and Phosgard®, have been shown to improve significantly PET flame-retardancy when used as comonomers. Phosgard incorporates a phosphorus atom within the main chain whereas Ukanol incorporates a phosphorus atom as a pendent substituent. Despite their acknowledged effectiveness, the mode of action of these fire retardants remains unclear, and in this paper we present a comparison of the overall thermal degradation behaviour of PET and Ukanol and Phosgard fire retarded formulations. DSC and particularly TGA data show that both Ukanol and Phosgard have some stabilising influence on PET degradation, especially under oxidative conditions. TGA and pyrolysis experiments both clearly indicate that neither additive acts as a char promoter. Only the Phosgard formulation shows any release of volatile phosphorus species which could act in the gas phase. On the other hand, the most striking feature of the pyrolysis experiments is the macroscopic structure of the chars produced by the fire-retarded formulations, which hints at their fire-retardancy action - an open-cell charred foam was obtained upon charring at 400°C or 600°C. This foaming layer between the degrading melt and the flame would lower the amount of fuel available for combustion, and would also limit the feedback of heat to the condensed phase.

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1. Introduction

According to UK Government statistics [1], over 600 people die in fires each year in the UK. Over 18,000 are injured, and fires in dwellings and commercial buildings are estimated to cost the UK economy £6900 million per annum [2]. In well over 50% of these fires, toxic fumes and smoke (in most cases evolved from polymeric materials) represent the sole or major contributing cause of death. Consequently, much work has been undertaken in reducing the flammability of polymeric materials.

Many types of fire-retardants are used in poly(ethylene terephthalate), PET, formulations, but the most common are additive phosphorus species like ammonium polyphosphate which enhances charring, or halogenated products used for their gas-phase action, inhibiting the ignition of the volatile pyrolysis products. Halogenated species are amongst the most effective fire-retardant species known, but are gradually being abandoned for environmental and safety reasons. Attention is therefore turned to phosphorus compounds, mostly under the form of reactive fire-retardants copolymerised with the polymer. Two commercial fire retardants, Ukanol$^{®}$ and Phosgard$^{®}$, have been shown to improve significantly PET flame-retardancy when used as comonomers. Phosgard incorporates a phosphorus atom within the main chain, whereas Ukanol incorporates a phosphorus atom in its side-groups. Both compounds are shown with their systematic nomenclature, and their repeat unit within PET in Table 1. They are used industrially for their fire-retardancy properties [3-5], but their mechanism of action, though studied in the past, is not clearly established.

In the late 1990s, the thermal and thermo-oxidative stability of Ukanol-containing PET was studied using thermogravimetric analysis (TGA) [6-8]. Under an inert atmosphere, Ukanol-modified materials showed lower thermal stability than PET, releasing volatiles at a slightly lower temperature (380°C vs. 417°C for PET). This was related to the cleavage of the weaker P-O and P-C bonds. However, the subsequent mass-loss of the fire-retarded polymer was very similar to that of PET, and no major structural changes were observed by NMR analysis. Under oxidative atmosphere, mass-loss was reported to occur at 380°C for both materials, and the main degradation process was found to occur more slowly with Ukanol. Slightly more char was obtained (+3-5%) for the fire-retarded polymer. These studies conclude that Ukanol has a solid-phase action in an oxidative atmosphere: the P-O bond would decompose at temperatures below PET, creating a phosphorus-rich residue which would limit the fuelling of

the flame. This residue would only decompose at higher temperatures than PET, yielding more char. The overall stability of the copolymer would not be greatly affected since the labile P-O bonds are situated in a side-group, and chains would retain their integrity.

However, the differences quoted in char yields in this study are comparable to experimental error on a TGA apparatus. While there is no doubt that Ukanol leads to an effective flame-resistant material, the mechanism proposed so far is not satisfactory. One could argue, for example, that the volatiles released early in the decomposition of Ukanol could play a gas-phase role never mentioned in the above papers.

Similar TGA studies have been conducted on Phosgard-containing copolymers of PET [6] under inert and oxidative atmospheres, showing a thermal destabilisation effect in both cases. This observation was related to the plasticizing effect of the phenyl side-group and the flexible P-O-C bond within the main chain [4,9]. Thermal destabilisation was further explained by the weakness of the P-O-C bond in the chain backbone, promoting earlier chain-scission. IR and NMR spectra of the degrading material showed a slight decrease of the integrations of the peaks associated with P=O, P-O-C and P-C bonds, which led the authors to conclude that phosphonate units were lost upon thermal degradation. However, the IR integrations only differed by 1-2%, which is once again well within experimental error for this technique.

In 2002 and 2003, Wu *et al* [10] and Zhao *et al* [11] studied the kinetics of thermo-oxidative degradation of Ukanol and Phosgard PET copolymers by non-isothermal TGA. This technique has been assessed by Holland and Hay [12], who showed that valid kinetic data could only be obtained in non-isothermal experiments for conversion below 50% of the initial mass: at higher conversions, the scheme of degradation includes too many side-reactions to fit the assumptions of the theories used. Taking this limitation into account, data from Wu and Zhao can still be used at low conversions. They found that under air, the activation energies (Ea) for mass loss were 180 kJ mol^{-1} for PET/Ukanol and 220 kJ mol^{-1} for PET/Phosgard, compared to 200 kJ mol^{-1} for PET. Ukanol could owe its lower activation energy to an easier degradation process involving the bulky side-groups only, yielding a phosphorus-rich oxidised layer on the surface of the material. Alternatively, early degradation of Ukanol could yield volatile radical species used in a gas-phase action to quench combustible volatiles evolved from the polymer. There is no suggestion as to why Phosgard should stabilise the polymer, given that P-C bonds (ΔH_f = -292 kJ mol^{-1}) are slightly weaker than C-C bonds

(ΔH_f = -347 kJ mol^{-1}), and in this case are present within the main-chain of the polymer. If anything, a similar destabilisation to that seen for Ukanol should be observed, which is what Chang *et al* [6] reported, without attempting to describe the kinetics of the process.

Most recently, Balabanovich [13] proposed a general phosphorus fire-retardancy mechanism involving a cyclic phosphinic anhydride additive, which would degrade via a cyclic phosphine (similar in structure to the precursor for Phosgard) into a solid residue and a high-boiling point trimethyl phosphine. He based his assertions on TGA experiments and spectrometric analysis of the volatile decomposition products and char obtained upon degradation. Such a mechanism combines vapour-phase and condensed-phase actions, and could potentially apply to the systems presented above.

This latest development suggests that the fire-retardancy mechanism involved for organic phosphorus compounds might not be as simple as suggested by other authors. The numerous observations reported on the degradation of PET containing Ukanol or Phosgard still do not provide definitive experimental evidence for any of the mechanistic pathways suggested. In this paper we present a comparison of the overall thermal degradation behaviour of PET and Ukanol and Phosgard PET formulations. In a subsequent paper, melt rheology and solid state NMR data will be presented and a mechanism proposed for the mode of action of the two retardants.

2. Experimental

2.1 Materials

PET (also called "PET-D25") and PET formulations containing Phosgard PF100 and Ukanol FR50/1 (respectively "PET-P" and "PET-U") were donated by the DuPont-Teijin Films$^{®}$ plant in Dumfries, Scotland. Upon elemental analysis, it was found that PET-P contained 0.6 ± 0.3% phosphorus by mass, and PET-U 0.5 ± 0.3% phosphorus by mass.

Unless otherwise stated, the materials were used as received (extruded chip), stored at room temperature and ambient humidity.

2.2 Instrumental Techniques

TG studies were carried out on a Shimadzu TA-50 instrument, with a heating rate of 10°C min^{-1} up to 500°C and a purge gas flow (air or nitrogen) of 20 mL min^{-1} were used.

DSC measurements were performed on a TA Instruments Q1000 series instrument, on 3 to 5 mg samples in aluminium pans, under a purge gas flow (air or nitrogen) of 40 mL min^{-1}, and with a heating rate of 10°C min^{-1}. DSC pan lids were pierced before use to facilitate volatile release and exposure of the sample to the purge gases.

The TVA line was built in-house following the descriptions by McNeill [14-16].The pumping system comprised an oil diffusion pump and a mechanical pump connected in-line; the vacuum reachable was 10^{-4} mbar at stable regime. Samples were heated from 50 to 600°C at 10°C min^{-1}. Volatile degradation products were initially trapped in two stages: a water-cooled cold ring (T ~ 12°C) just outside the heated zone condensed the high-boiling point materials, and a liquid nitrogen-cooled trap (T ~ -196°C) collected the low-boiling point species further down the line. Low-boiling point products were subsequently distilled slowly from the trap, and collected as three fractions in different lines downstream, to be analysed by gas-phase FTIR. Cold-ring products were collected and analysed by FTIR and ^{1}H-NMR. Linear-response Pirani pressure gauges along the set-up recorded the pressure changes as volatiles were evolved from the degrading products and pumped through the system into cold traps.

Charring experiments were conducted under a flow of nitrogen or air. 1 g of each polymer was placed in a ceramic sample boat, introduced in a pyrolysis tube, and submitted to pyrolysis at 5°C min^{-1} to 600°C under a flow of nitrogen or air at 50 mL min^{-1}. Again the heating rate was very slow, and was chosen to match that of the solid-state NMR experiment (limited by the experimental set-up) described in a following paper.

An FTIR Mattson 5000 was used in transmission mode, to record spectra from films of polymer and solid degradation products on NaCl discs, or of volatile degradation products in the gas-phase.

The NMR instruments used for the charcterisation of degradation products in deuterated chloroform solution were a Bruker DPX400 instrument (^{1}H) and a Bruker DX200 at the University of Nottingham (^{31}P).

3. Results and Discussion
3.1 Thermogravimetry

The TGA traces for all three polymers under nitrogen can be seen in Figure 1.
No difference can be seen in the behaviour of the three polymers, except for a slight delay in the initial volatile release for PET-U. Mass loss reaches 95% at 403°C for PET-U, and at 396°C for PET and PET-P. The mass loss profiles are identical, with the PET-U samples retaining a slightly higher mass, which always stays within the 4% experimental error boundary for this technique.

Under air, differences appear between the behaviours of the three polymers (Figure 2). The sample mass reaches 95% at 381°C for PET, which is 10 to 14°C before PET-P or PET-U. All through the heating program, the fire-retarded samples retain a similar or higher mass than pure PET. At 430°C, for example, PET-U samples retain 75% of their initial mass, while PET samples retain 66%. Under air, PET and PET-U display a two-step mass-loss profile, with an initial slow mass loss followed by a step of high mass loss rate. PET-P, however, shows a third process occurring between the two already described: a slightly faster evolution of volatiles up to about 430°C, where the rate of mass becomes similar to that of the other two materials.

Surprisingly, ultimate char yields are very similar for all three materials, where the usual mechanism of reaction for phosphorus fire-retardant species involves a much heavier char (30-40% of the initial mass).

However, this data was generated on very small samples of around 10 to 15 mg, which do not necessarily represent the real behaviour of polymers in a fire situation. The heating rate chosen is also very slow compared to real fires, but the usual value of 10°C min^{-1}was necessary to compare our results with other sets of data, and to have some consistency between the different techniques.

3.2 Differential Scanning Calorimetry

DSC results can show the net thermal outcome of degradation reactions, and therefore relate to the mechanism of action of fire-retardants. A solid-phase action would induce more charring, so a high number of bonds formed and a largely exothermic process. A purely gas-phase action would require the production of a large amount of volatiles species and the breaking of many chemical bonds, which is an endothermic process.

All three materials give rise to globally similar thermograms. Degradation is endothermic under nitrogen and exothermic under air, with extensive release of volatiles (spikes on the peak slopes). Overlaid thermograms obtained for the polymers under nitrogen and air are shown in Figures 3 and 4 respectively.

Differences between the thermograms are mainly noticeable for the degradation peak. The earliest point after melting where the baseline shifts significantly is taken as the T_{shift} value, which represents the initial phenomena of degradation. The peak onset temperature and the peak maximum temperature are noted $T_{peak\ onset}$ and $T_{peak\ max}$ respectively. These values are quoted in Table 2.

In particular, T_{shift} is higher for Ukanol formulations compared to PET, both in nitrogen and air. The fire-retardant seems to prevent the early extensive bond breakage, which would lower the amount of volatiles emitted initially. Baseline shift is delayed until a temperature 20°C higher than that for PET is reached, under both atmospheres. Phosgard seems to act later than Ukanol in the degradation process, as its main effect is seen on the degradation peak onset (26°C lower than for PET). The shape of the degradation peak is also different, with an initial exothermic event at 357°C, before extensive volatile evolution takes place, and a main peak maximum found at much higher temperature than for PET. Comparatively, PET-U behaves quite similarly to PET after the initial baseline shift. Volatiles emission (spikes observed on the signal) seems to be initially less extensive for PET-U.

These results highlight that Phosgard and Ukanol probably have different mechanisms of degradation, and that these differences are more apparent under oxidative conditions. The presence of oxygen leads to an initial exothermic process in PET-P, which could be crosslinking of the chains or chain scission by extensive oxidation, followed by a second much more important exothermic process that stretches up to 500°C, much higher than the other two formulations.

3.3 Thermal volatilisation analysis

From the TGA and DSC experiments it can be seen that the fire-retarded formulations delay the release of volatiles from the degrading polymer. Thermal volatilisation analysis is a powerful tool to study the volatiles released by degrading polymers under vacuum, in a purely non-oxidative system, which can still be relevant for the interpretation of oxidative behaviour. The distillation of the volatiles from the main trap was followed using a Pirani pressure gauge, and a thermocouple. The resultant pressure vs temperature profiles are shown in Figures 5 and 6.

In all three cases, the volatiles were identified by gas-phase FTIR as CO_2, (fraction 1), acetaldehyde (fraction 2) and water (fraction 3). The higher boiling-point volatiles (cold-ring fraction) were also collected and analysed by FTIR, with Table 3 giving the peak assignments for that of PET. The predominant species in terms of intensity of the peaks is the PET structure, which is likely to be encountered as oligomers (linear or cyclic) evolved from the degrading melt. Also present are vinyl benzoate and carboxylic acid end groups from the ester β-scission process. The ^{1}H-NMR spectrum (Figure 7) shows that the main species in the cold ring fraction is the PET repeat unit (aromatic CH δ=8.06 ppm, aliphatic CH_2 δ=4.67 ppm). Also present are benzoic acid chain ends (acid OH δ=13.3 ppm, aromatic CH quintuplet δ=8.14 ppm), and vinyl benzoate groups (three aromatic multiplets at δ=7.64, 7.52, 7.43 ppm, two aliphatic CH=CH doublets at δ=5.17 ppm and δ=4.86 ppm). Other aromatic species exist in the sample, according to minor peaks between 7.7 and 8.0 ppm, which may be methyl benzoate or methyl terephthalate. These assignments are less certain than the well-defined assignments for PET fragments and terephthalic acid groups.

PET-P and PET-U show similar cold-ring fractions to PET, according to FTIR (oligomers, vinyl benzoate and benzoic acid chain ends) and ^{1}H-NMR in d_6-DMSO (same peaks as for PET, plus a singlet at 8.31 ppm). ^{31}P-NMR did not give rise to any signal, indicating that this ^{1}H-NMR peak at 8.31 ppm does not originate form a phosphorus structure. It can however be assigned to the aromatic –H of terephthalic acid (TPA), not observed in the PET cold-ring fraction. No phosphorus species were detected amongst the volatile products from any of the TVA samples.

Analysis of the TVA experiments reveals that the structure of the degradation products under vacuum is identical for PET and its fire-retarded formulations, except for the presence of TPA in the cold-ring fraction of the fire-retarded polymers. Two theoretical mechanisms could apply. On the one hand, a restriction in the mobility of the polymer chains, due to the fire-retardant units, could restrict chain scission mechanisms to chain-ends which are not engaged in cross-links. This would yield much smaller segments than for simple PET, and more opportunities for liberating TPA amongst the volatile products from fire-retarded formulations. On the other hand, the formation of TPA could be catalysed by the presence of phosphorus in both fire-retarded formulations, through a degradation mechanism where the phosphorus centre could act as a catalyst for TPA release.

TVA pressure and spectroscopy data indicate that under vacuum, the degradation mechanisms and products of PET, PET-P and PET-U are virtually identical. Rather than having a major char-forming action, the presence of TPA monomer in the products from the fire retarded samples suggests, in fact, that fragmentation is more pronounced in these samples than in PET. On the other hand, no specific species is evolved that could account for an intrinsic gas-phase fire-retardancy action.

3.4 Dynamic pyrolysis

Table 4 summarises the char yields obtained in dynamic pyrolysis (5°C min^{-1} to 600°C) of PET, PET-U and PET-P. The char yields are very similar for all three formulations, and far from the 30 to 40% expected if Ukanol and Phosgard behaved like typical phosphorus fire-retardants. Coupled with the TVA and TGA data, this indicates that neither Ukanol nor Phosgard act as charring enhancers, and their fire-retardancy mechanism is therefore not of the kind usually ascribed to phosphorus species.

The appearance of the chars was unusual. After reaching 600°C, the char obtained for PET covered the walls of the boat in a black, glossy and homogeneous layer. The chars for both fire-retarded formulations were very structured, in a three-dimensional network all over the boat cavity, like a foam with open cells.

In a separate series of pyrolysis experiments, about 3 g of each formulation was introduced into pyrolysis test tubes, and submitted, under static air, to a heating program of 7°C min^{-1} (on average) up to 400°C, and this temperature held for 25 minutes. The degrading polymers were observed by pulling the tubes out of the block heater for a few seconds at a time. The overall behaviour was very similar for all three materials. The pellets would start to melt around 270°C, and be completely molten at 310°C, at which temperature small bubbles appear on the walls of tube in the melt. The viscosity of PET-P was visibly lower than that of PET-U and PET upon tilting the tube. At 345°C, the surface of the melts started to become yellow, and the colour propagated to the entire melt from 360°C. At that point, there were more bubbles in pure PET than in PET-U, and PET-P contained almost no bubbles until reaching 375°C. From 380°C, a large amount of white fumes started to evolve, with some material recondensing on the walls of the tubes. After reaching 400°C, volatile evolution continued, and the discolouration of the melts was more and more pronounced, until a very dark froth appeared at the surface of the melts after 5 minutes. The foaming phase was higher in the tube for fire-

retarded PET than for pure PET, and remained so all along the subsequent degradation. After 25 minutes at 400°C, the tubes were allowed to cool within the block heater. The tubes recovered after cooling all contained, from bottom to top, a succession of characteristic layers in different amounts. At the bottom of the tube was a closed glossy black char, topped by an open-cell foamy layer of black charred polymer. Above the limit of the heated part of the tube, volatiles had recondensed, and two types were observed: a white layer covered the walls, while yellow solid has agglomerated in small hillocks around the inside of the tube. The main difference between the fire-retarded formulations and the pure PET was the height of the foam layer: it consistently reached the height of 7 cm for the fire-retarded PET materials, while in normal PET it barely reached 5 cm. Phosgard and Ukanol therefore induce the production of a much more structured and foamed char, but in a similar amount to that observed for PET: the quality, and not the quantity of the chars, is modified.

Chars from both sets of experiments were submitted for elemental analysis (C, H and P contents). Results are reported in Table 5, where all results have an intrinsic experimental error of $\pm$ 0.3 wt%. The final column shows the ratio of carbon to phosphorus contents for the fire-retarded polymers. These values indicate that under nitrogen, both fire-retarded polymers release comparatively more C than P (final ratio inferior to initial ratio). However, under air, the PET-P char shows a carbon / phosphorus ratio more than double the initial value, showing that a lot more phosphorus has been evolved from the material than carbon. PET-U, on the other hand, does not seem as affected and retains a carbon / phosphorus ratio close to the initial value. We note, however, that the error on the P content is large relative to the quantities of P present.

These results suggest that phosphorus is released in a larger proportion in the volatile products of PET-P polymers under thermo-oxidative conditions. The recondensed volatile degradation products should therefore contain at least some of the phosphorus evolved. To investigate this, the high boiling-point volatiles from the pyrolysis under air were characterised by elemental analysis (see Table 6). Further characterisation by ^{1}H-NMR in d_6-DMSO solution revealed the characteristic peaks for terephthalic acid, di- or mono-methyl terephthalate, PET oligomers and an aldehyde species (δ=10.11 ppm). Although the nature of the products was similar, the proportions present differed, as indicated by the peak integrations. With reference to the PET spectrum, PET-U volatiles contained more terephthalic acid and methyl

terephthalate, and less oligomer. PET-P volatiles contained mostly terephthalic acid, and less oligomer and methyl terephthalate than for PET. This is similar to the TVA degradations. An example of a spectrum is shown in Figure 8 for PET.

^{31}P-NMR was also run on the volatile samples from PET-U and PET-P. The former did not give rise to any signal (in agreement with the microanalysis data), while the latter displayed three small resonance peaks (δ=25.32 ppm, 13.33ppm, -0.46 ppm) when decoupled from ^{1}H as shown on Figure 9. The chemical shifts are tentatively assigned, from data by Kirby [17], to the large family of tetrahedral phosphorus compounds. This is too vague to be of use in the determination of specific structures, but nevertheless proves that some phosphorus species are evolved from PET-P under thermo-oxidative pyrolysis.

These pyrolysis experiments on bigger samples than those used in TGA, DSC or TVA reveal that the fire-retarded formulations do not produce a higher amount of char, but rather a more structured char, which hints at their fire-retardancy action.

4. Conclusions

DSC and particularly TGA data show that both Ukanol and Phosgard have some stabilising influence on PET degradation, especially under oxidative conditions. TGA and pyrolysis experiments both clearly indicate that neither additive acts as a char promoter. Only the Phosgard formulation shows any release of volatile phosphorus species which could act in the gas phase. On the other hand, the most striking feature of the pyrolysis experiments is the macroscopic structure of the chars produced by the fire-retarded formulations, which hints at their fire-retardancy action: an open-cell charred foam was obtained upon charring at 400°C or 600°C. This foaming layer between the degrading melt and the flame would lower the amount of fuel available for combustion, and would also limit the feedback of heat to the condensed phase.
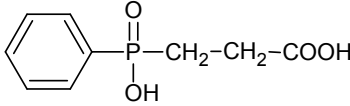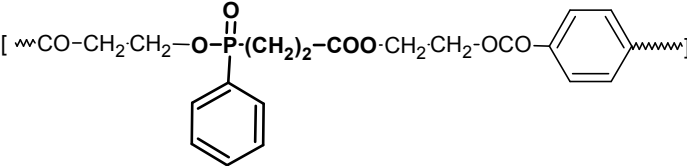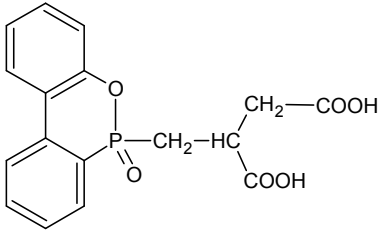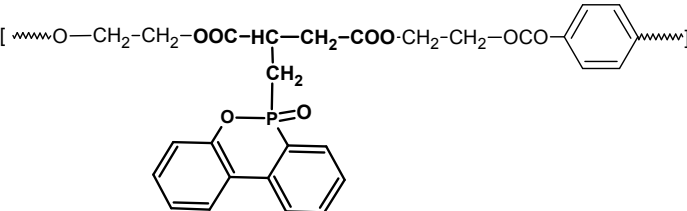
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Tables (six)

Fire-retardant	Repeat unit in PET
Phosgard® 2-carboxyethyl(phenyl phosphinic) acid	[ᵐCO−CH₂·CH₂−O−P·(CH₂)₂−COO·CH₂·CH₂−OCO− ᵐ]
9,10-dihydro-10-[2,3-di(hydroxy carbonyl) propyl] 10-phosphaphenanthrene-10-oxide Ukanol®	[ᵐO—CH₂−CH₂−OOC−HC−CH₂−COO·CH₂−CH₂−OCO− ᵐ]

Table 1: Ukanol® and Phosgard® structures

Atmosphere	Material	T_{shift} (°C)	$T_{peak\ onset}$ (°C)	$T_{peak\ max}$ (°C)
N$_2$	PET	338	371	442
	PET-P	344	380	434
	PET-U	358	380	439
Air	PET	310	360	444
	PET-P	309	346	480
	PET-U	331	357	447

Table 2: Summary of key DSC degradation temperatures for the three polymer systems.

Frequency / cm^{-1}	Absorption mode	Compound assignment
3062, 2960	Aromatic CH stretching	PET
2693, 2557	Aliphatic CH$_2$ stretching	PET
1793	Fingerprint	PET
1720	C=O stretching	PET
1687	C=O stretching	Benzoic / terephthalic acid
1265	CO-O stretching	Vinyl benzoate
1248	CO-O stretching	PET
1132	CO-O bending	PET
1097	CO-O bending	Vinyl benzoate
1018, 874	Para-substituted benzene	PET
947	Out of plane bending O-H	Carboxylic acid
727	Disubsituted benzene ring	PET / terephthalic unit

Table 3: IR peaks and assignment for PET D25 cold ring fraction from TVA.analysis.

	PET	PET-P	PET-U
Nitrogen	17.9%	21.4%	23.0%
Air	0.3%	2.2%	1.5%

Table 4: Pyrolysis char yields in dynamic N_2 and air for the three polymer systems (5°C min^{-1} to 600°C).

Conditions	Material	% C	% H	% P	%C / %P
Initial	PET	62.7	4.1	0	*N/A*
	PET-P	62.5	4.1	0.6	*104.2*
	PET-U	62.6	4.0	0.5	*125.2*
Tubular furnace 600°C, N_2	PET	92.7	3.3	0	*N/A*
	PET-P	93.5	3.5	1.1	*85.0*
	PET-U	90.4	3.0	2.7	*33.5*
Block heater 400°C, air	PET	63.7	3.7	0	*N/A*
	PET-P	65.0	3.9	0.3	*216.7*
	PET-U	66.1	4.1	0.7	*94.4*

Table 5: Elemental analysis for chars of PET and fire-retarded PET from pyrolysis experiments (5°C min^{-1} to 600°C under N_2 or 7°C min^{-1} to 400°C under air).

Material	% C	% H	% P
PET	58.8	3.5	0
PET-P	58.5	3.6	1.3
PET-U	58.4	3.6	trace / nil

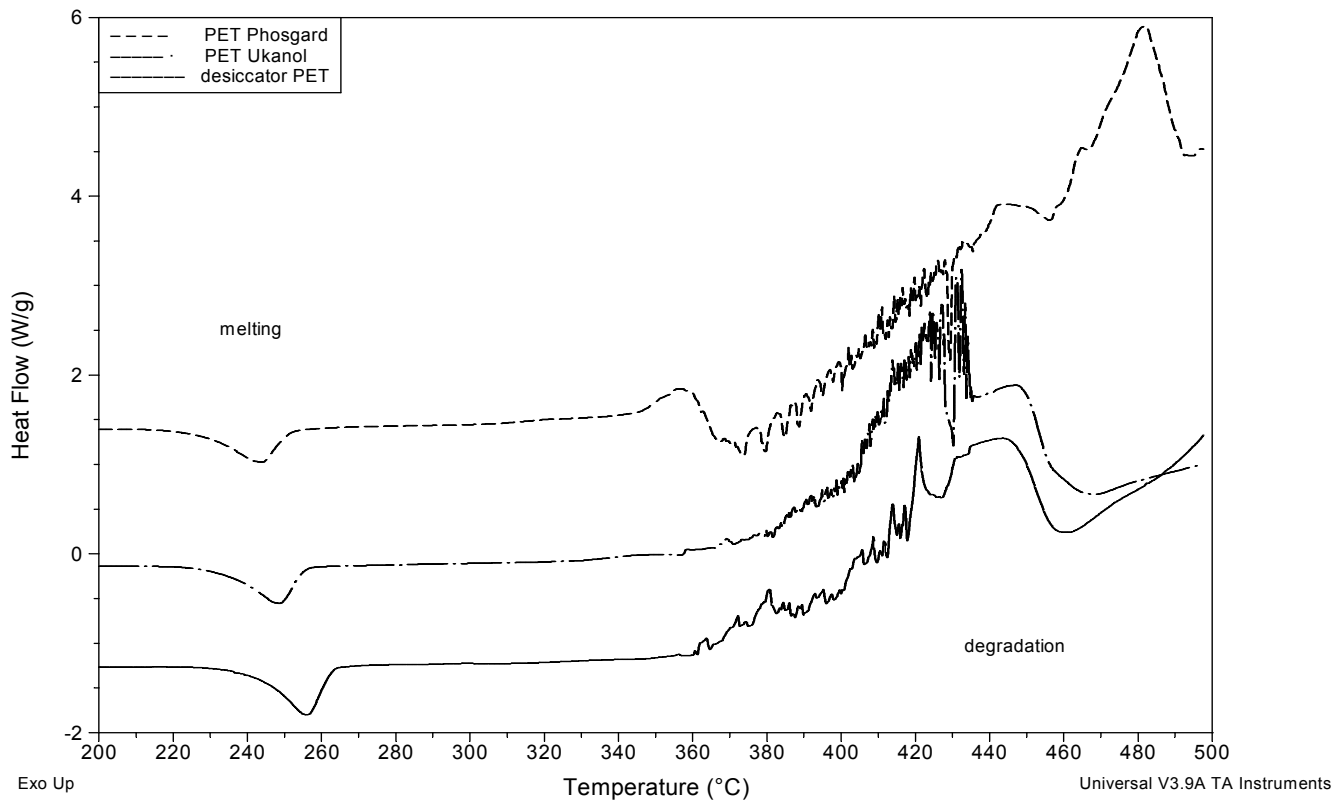**Table 6:** Elemental analysis of high boiling volatile products from PET, PET-P and PET-U pyrolyses in air ($7^{o}C$ min^{-1} to 400°C).

Figure 1: TGA Thermograms for the three PET polymers (N_2, 10^oC min^{-1}).
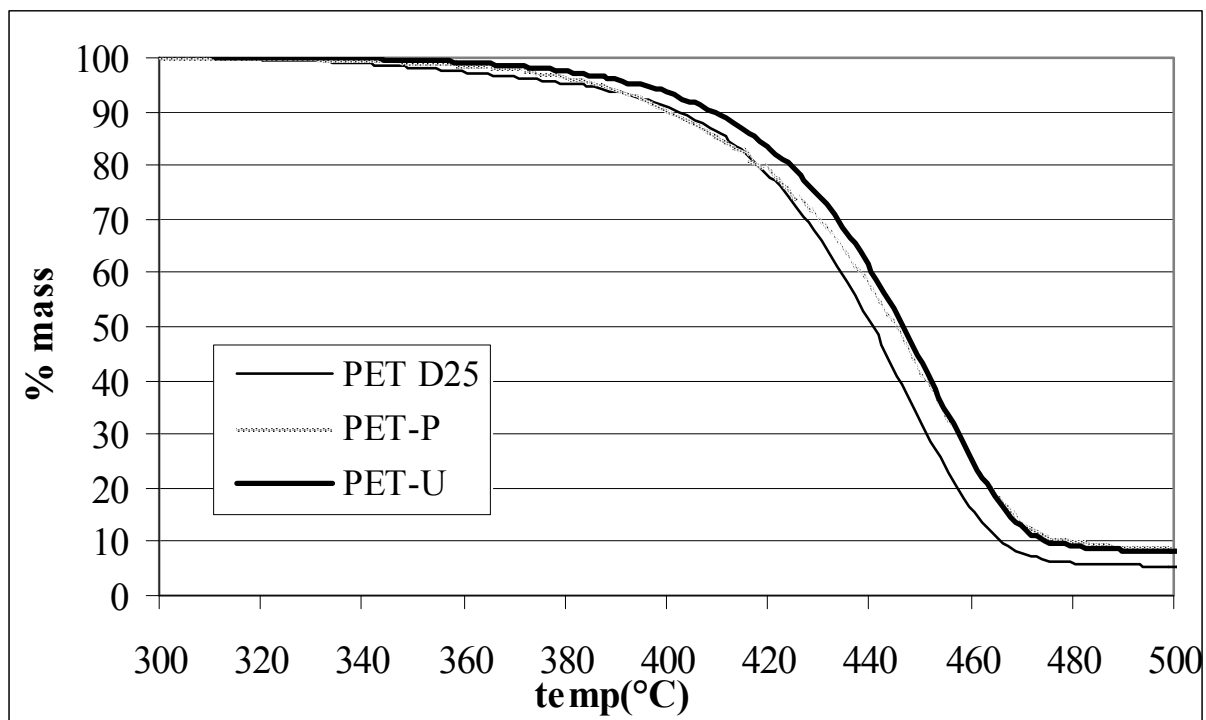
Figure 2: TGA Thermograms for the three PET polymers (air, 10^oC min^{-1}).
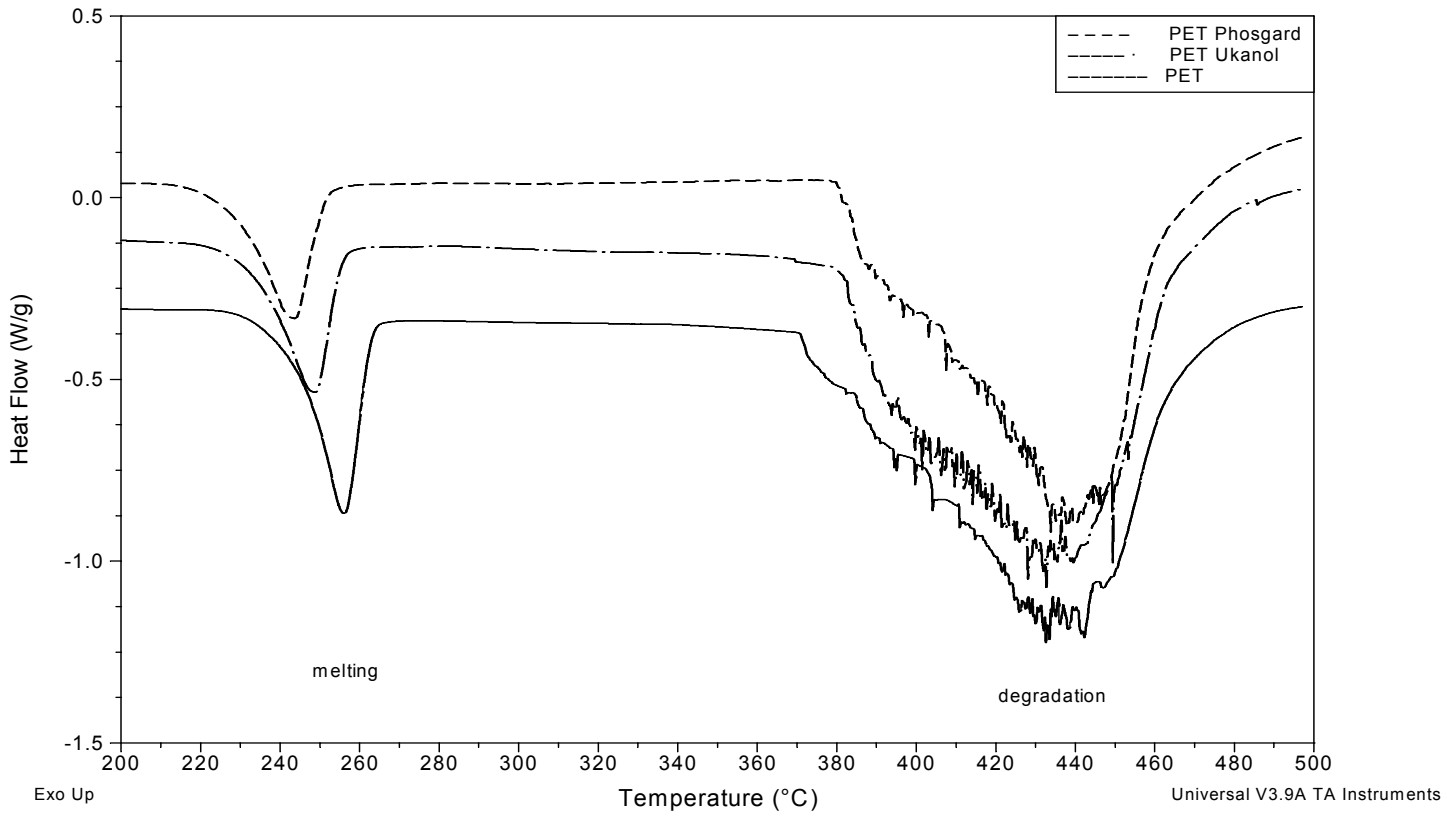
Figure 3: DSC thermograms for the three PET polymers (N_2, 10^oC min^{-1}).

**Figure 4:** DSC thermograms for the three PET polymers (air, 10^oC min^{-1}).
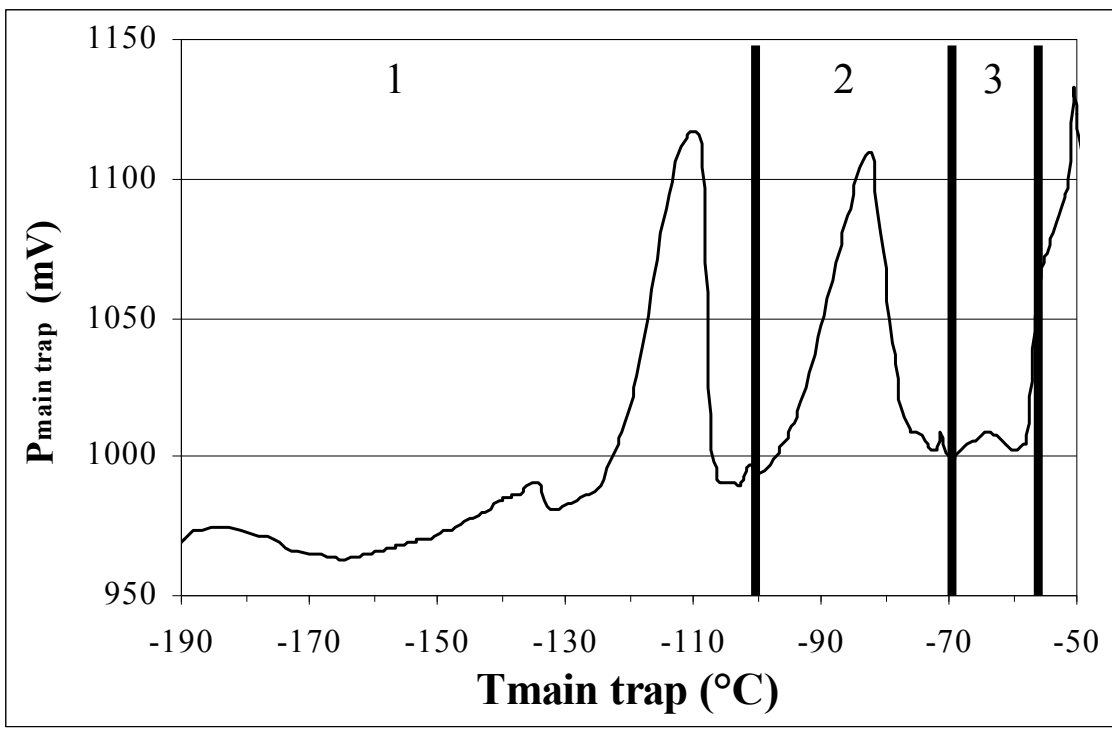
Figure 5: Pressure at sub-ambient trap during sub-ambient distillation of volatile products for PET-D25. Vertical lines indicate the divisions between fractions collected for subsequent IR analysis.
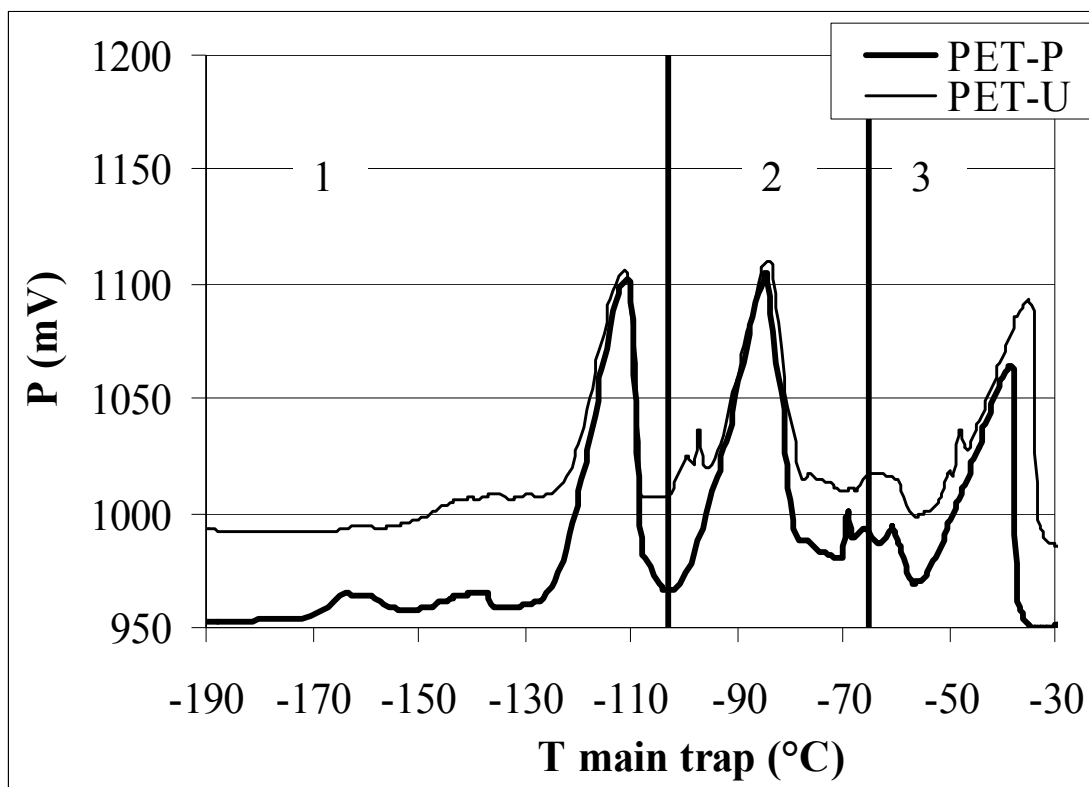
Figure 6: Pressure at sub-ambient trap during sub-ambient distillation of volatile products for PET-P and PET-U. Vertical lines indicate the divisions between fractions collected for subsequent IR analysis.
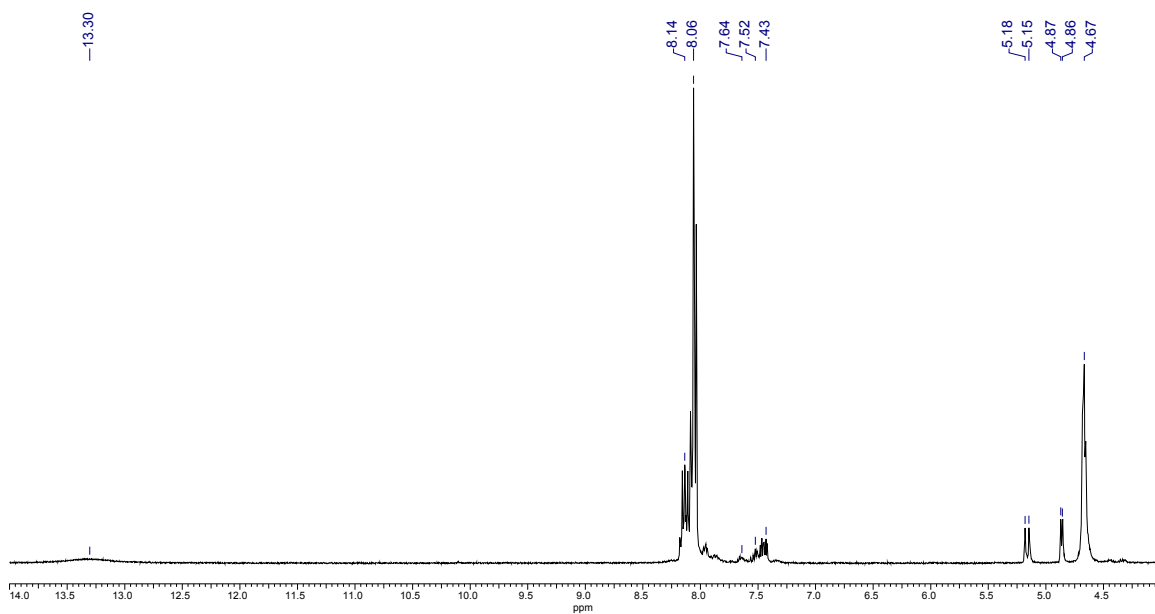
Figure 7: Portion of ^{1}H-NMR spectrum, PET-D25 TVA cold ring fraction in d_6 DMSO.
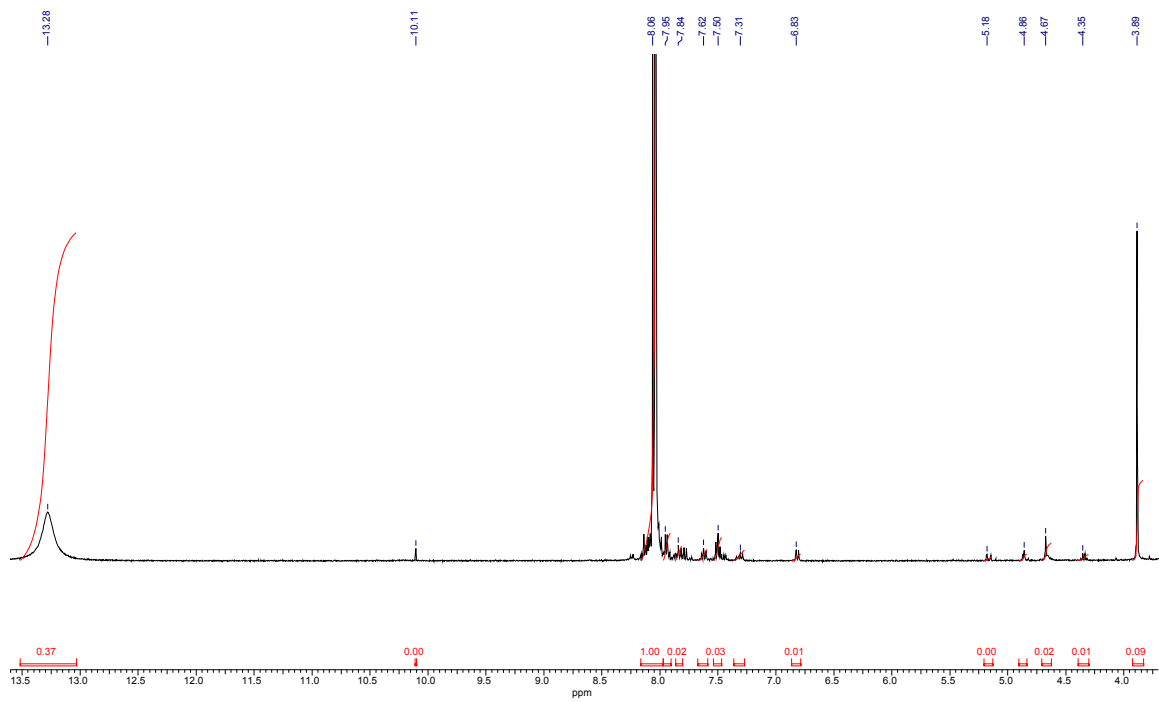
Figure 8: ^{1}H-NMR of condensed volatiles from PET-D25 block-heater pyrolysis in air (7°C min^{-1} to 400°C).

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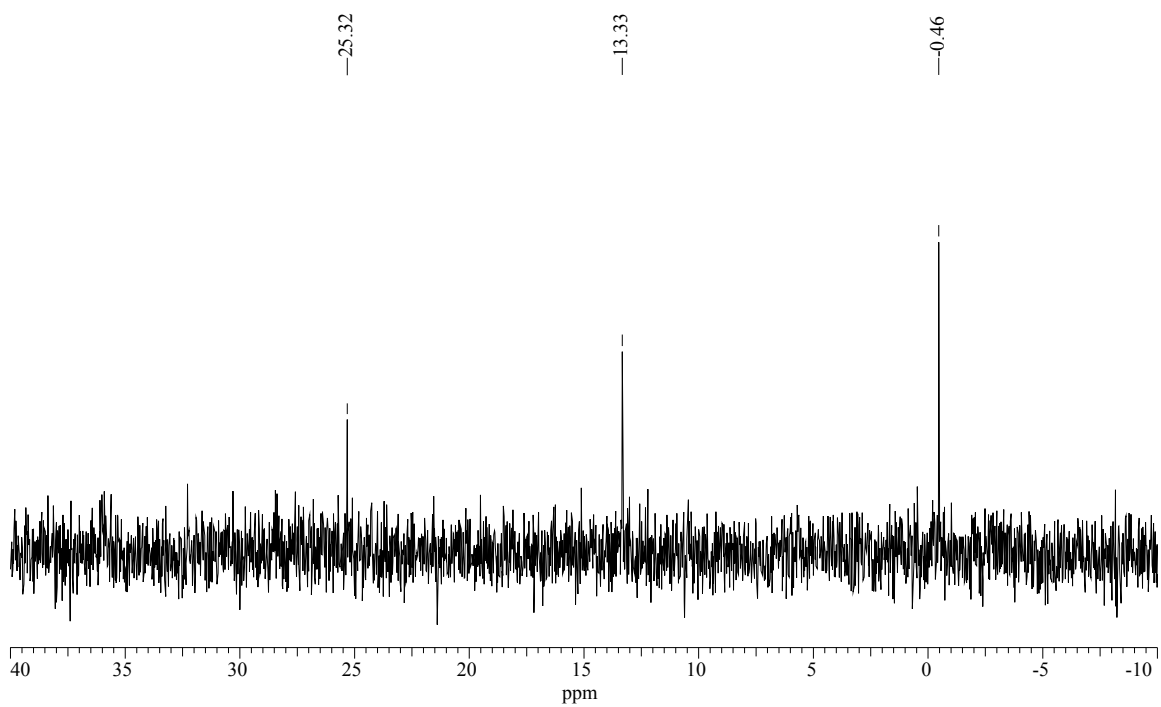
Figure 9: ^{31}P-NMR of condensed volatiles for PET-P block-heater pyrolysis pyrolysis in air (7°C min^{-1} to 400°C).