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PRODUCTS OBTAINED DURING COMBUSTION OF POLYMERS UNDER SIMULATED INCINERATOR CONDITIONS

II. POLYSTYRENE

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SUMMARY

The products from polystyrene combustion at temperatures of 800–950°C are described. Products consisted of a complex mixture of polycyclic aromatic hydrocarbons from alkyl benzenes to benzo[ghi]perylene. Compounds were identified by capillary gas chromatography–mass spectrometry and quantitated using capillary gas chromatography.

INTRODUCTION

Our interest in combustion products of polymers has arisen because of the complex organic mixtures identified in combustion effluents. Compounds such as polycyclic aromatic hydrocarbons (PAHs) have been identified in effluents from coal combustion and municipal incineration^{1–6} and have been identified on fly ash from municipal incinerators⁷. Plastics are one of the components of municipal waste, averaging approximately 4–5% of the total composition^{8–11}. However, little study has been performed on individual polymers. Although the exact composition of the plastics contained in municipal waste is unknown, the high production of polystyrene combined with increased use in food containers^{11–13} assures that it will be contained in the waste stream.

Much of the past work involving polystyrene combustion has used techniques such as thermogravimetric analysis or differential scanning calorimetry to follow the weight loss over time at various temperatures, with little concern for degradation

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products produced¹⁴⁻¹⁶. In recent work on pyrolysis of polystyrene at 540°C very few degradation products were identified, and consisted mainly of styrene, substituted methyl- or ethylstyrene, and styrene dimers and trimers¹⁷. Studies by Boettner *et al.*¹⁸ on polystyrene combustion at temperatures below 580°C have found largely styrene, along with other components. These were identified by gas chromatography (GC) and IR as largely benzene-containing species such as toluene, ethylbenzene, benzaldehyde, phenol, indene, naphthalene and biphenyls. Pyrolysis at 500°C in helium resulted in the identification of 16 compounds, again using GC and IR. These compounds were phenyl-substituted alkanes and alkenes, with hydrocarbon chain lengths from four to six carbons and containing up to three phenyl groups and varying unsaturation in the carbon chain. Mechanisms for formation of the various products were proposed, all involving radical formation and subsequent decomposition¹⁹.

Gas chromatography-mass spectrometry (GC-MS) analysis of the combustion products produced below 490°C has been reported by Masarik *et al.*²⁰. Samples (2.5 g) of various flame-retarded polystyrenes were combusted in a Setchkin apparatus, which allows direct trapping of combustion effluents. The compounds identified were benzene, toluene, ethylbenzene, styrene, propylbenzene and aldehydes such as benzaldehyde and phenylacetaldehyde, and agreed with results obtained by previous researchers^{21,22}.

Other studies involving polystyrene degradation have focussed on the formation of soot during combustion. Upon combustion of polystyrene at temperatures between 600 and 900°C, several PAHs were extracted from the soot produced. Polystyrene was found to evolve three to four times as much soot as polyethylene, but with smaller amounts of organics present in the soot²³. At 900°C, the weight of soot produced from polystyrene was almost 50% of the initial polymer weight. Work of Pasternak *et al.*²⁴ supports the statement that polystyrene produced three times as much smoke; in addition, it was found that flaming combustion produced largely 3- and 4-ring aromatic species, with polystyrene producing the greatest amount of extractable organics in both flaming and non-flaming modes.

Our approach involved the use of capillary GC and GC-MS to identify combustion products collected in liquid nitrogen cold traps and on pyrex wool, allowing us to obtain both qualitative and quantitative information. Combustion at several different temperatures permitted an examination of the effect of temperature on both amount and type of species formed.

EXPERIMENTAL

Polystyrene was obtained in pellet form, density 1.047, glass transition temperature 100°C, melting temperature 237.5°C, from Aldrich (Milwaukee, WI, U.S.A.). Standard solutions for evaluation of GC and GC-MS performance, the combustion apparatus and GC and GC-MS analyses and have been described in detail elsewhere^{25,26}.

RESULTS AND DISCUSSION

Combustion of polystyrene resulted in the production of a complex mixture of PAHs. Over 90 different compounds were identified in the combustion effluents

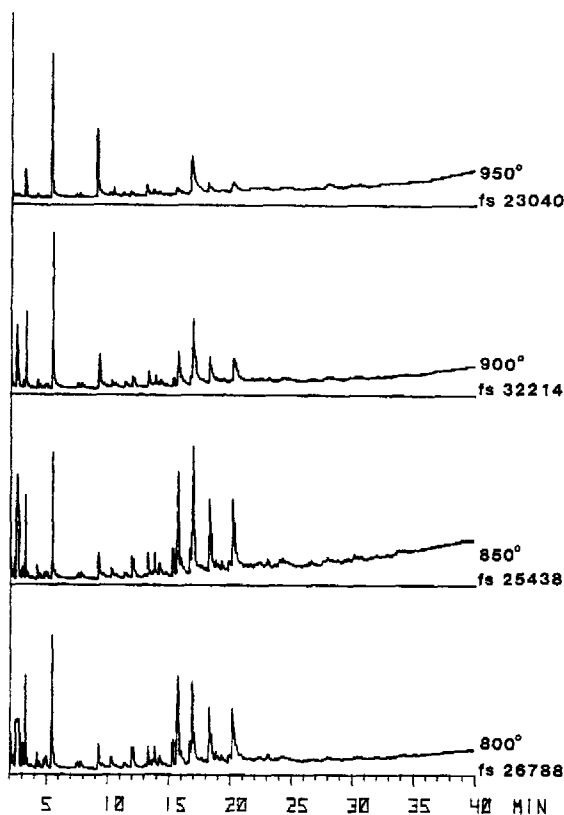


Fig. 1. Total ion chromatograms from polystyrene cold trap extracts at differing combustion temperatures. Combustion temperature and full scale values given in right hand margin.

from polystyrene. Polystyrene combustion produced large numbers of substituted aromatics, along with a generally complex mixture of condensed ring compounds.

Cold traps

The total ion chromatograms (TIC) for the cold trap extracts of polystyrene combustion at the various temperatures are presented in Fig. 1. There is an obvious decrease in the amounts of the various species formed as the temperature increases from 800 to 950°C. The 800°C sample has *ca.* 12 major components, while at 950°C there appear to be only four significant peaks. At combustion temperatures below 950°C, there appear to be eight major peaks; a series of three peaks at 2.5, 3.5 and 5.5 min, a smaller peak at 9 min, and a group of four larger peaks in the region between 15 and 21 min. At 950°C, the peaks at 3.5, 5.5, 9 and 17 min are all that remain. These correspond to indene, naphthalene, biphenyl and phenanthrene, respectively. The components which have been lost are methylstyrene, (*p*-methylphenyl)phenylacetylene, 1-phenylnaphthalene, and 2-phenylnaphthalene. At a combustion temperature of 950°C, only 33 compounds are detected by GC-MS analysis, while at lower temperatures between 40 and 50 different compounds are identified.

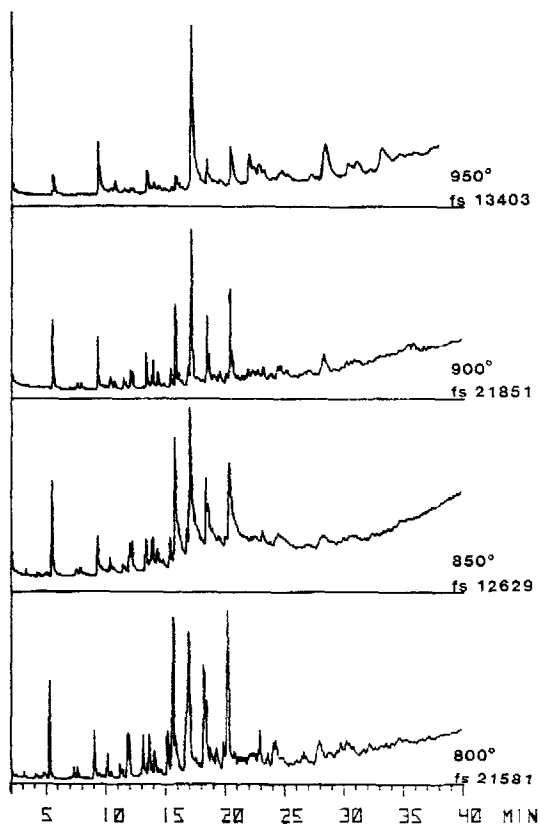


Fig. 2. Total ion chromatograms from polystyrene glass wool trap extracts.

Many of the compounds identified in the cold trap extracts are substituted benzenes: for example 1-, 2-, and 3-phenylpropene; *o*-, *m*-, and *p*-methylstyrene, and up to four $C_{10}H_{10}$ isomers are found at the various temperatures. In addition, 1- and 2-methylnaphthalene, the various monomethylated biphenyls, methylfluorenes and methylphenanthrenes and anthracene are found. The most noticeable feature of polystyrene combustion is the large numbers of PAHs formed. These larger numbers of PAHs are found mostly in the glass wool extracts, while the cold trap extracts contain mainly the lighter components, especially the substituted phenyls, biphenyls, and 2-ring aromatic compounds.

Glass wool traps

Fig. 2 shows the TIC of the glass wool extracts from polystyrene combustion. Again, as temperature increases we see a drop in the number of components observed. There appear to be a large number of components present at low levels, as evidenced by the jagged baseline in the 800°C sample. Here, the baseline is only really flat at the beginning of the chromatogram, between naphthalene at 5.5 min and the methylnaphthalene doublet at 7.4–7.8 min, and then again after that to biphenyl at 9 min.

The compounds identified in the glass wool extracts are a complex mixture of

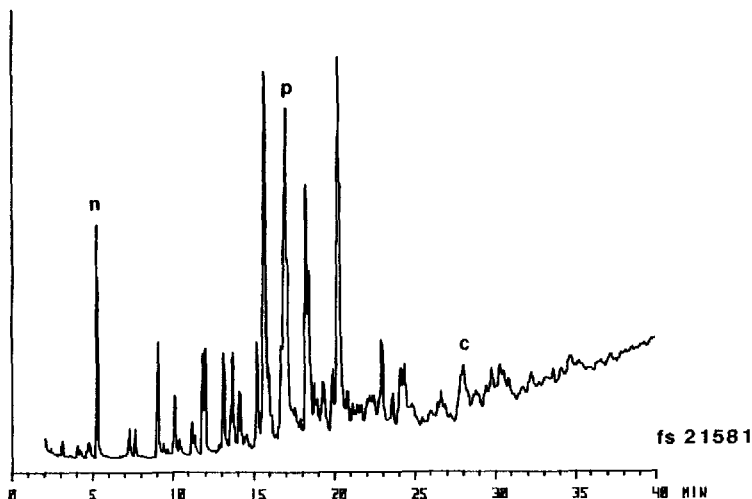


Fig. 3. Total ion chromatogram from polystyrene 800°C glass wool extract. Peak marked n is naphthalene; p is phenanthrene; c is chrysene.

polycyclic aromatics. Fig. 3 is an expanded plot of the TIC from the 800°C sample. This sample contained almost 70 compounds which were detected by GC-MS and over 180 compounds detected in analysis by capillary GC-flame ionization detection (FID). Very few compounds which elute prior to naphthalene are detected, while many of the species identified have molecular weights and chromatographic retention times greater than phenanthrene (mol. wt. 178; retention time 17 min).

Compounds which were identified included the methylnaphthalenes and the methylbiphenyls (2-, 3-, and 4-), methylfluorenes, vinylnaphthalenes, diphenylethene

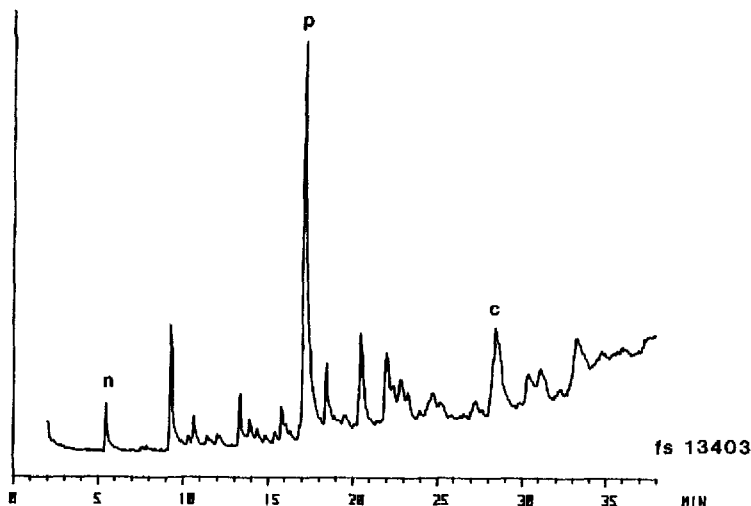


Fig. 4. Total ion chromatogram from polystyrene 950°C glass wool extract. Peak marked n is naphthalene; p is phenanthrene; c is chrysene.

TABLE I
COMPOUNDS IDENTIFIED IN COMBUSTION OF POLYSTYRENE

× means present in that sample. T = Cold trap extract. GW = Glass wool extract.

Compound	800°C		850°C		900°C		950°C	
	T	GW	T	GW	T	GW	T	GW
3-Phenylpropene			×					
2-Propenylbenzene	×			×				
Benzaldehyde	×							
<i>m</i> -Methylstyrene			×					
<i>p</i> -Methylstyrene	×		×			×		
<i>o</i> -Methylstyrene		×		×		×		
1-Propenylbenzene	×		×	×				
Indane	×							
Indene	×	×	×	×	×	×	×	
Methylpropenylbenzene	×							
Methylindane	×							
C ₁₀ H ₁₀ , isomer No. 2	×		×					
C ₁₀ H ₁₀ , isomer No. 3		×	×	×		×		
C ₁₀ H ₁₀ , isomer No. 9	×		×					
C ₁₀ H ₁₀ , isomer No. 4		×		×		×		
C ₁₀ H ₁₀ , isomer No. 8	×		×					
C ₁₀ H ₁₀ , isomer No. 5		×		×				
Azulene	×	×	×	×	×		×	
C ₁₀ H ₁₀ , isomer No. 6	×		×					
C ₁₀ H ₁₀ , isomer No. 7				×				
Naphthalene	×	×	×	×	×	×	×	×
2-Methylnaphthalene	×	×	×	×	×	×	×	
1-Methylnaphthalene	×	×	×	×	×	×	×	
Biphenyl	×	×	×	×	×	×	×	×
2-Methylbiphenyl	×	×						
1-Vinylnaphthalene		×						
2-Vinylnaphthalene		×				×	×	
Diphenylmethane	×	×	×	×	×			
Acenaphthylene	×	×		×	×	×	×	×
4-Methylbiphenyl	×	×	×	×	×	×	×	×
3-Methylbiphenyl	×	×			×			
1,1-Diphenylethene	×	×	×	×	×	×	×	×
1,2-Diphenylethene	×	×	×	×	×	×		
Unknown, MW 194	×	×						
Fluorene	×	×	×	×	×	×	×	×
Unknown, MW 194	×	×				×		
9-Methylfluorene	×	×	×	×	×	×	×	×
1,3-Diphenylpropane		×						
Diphenylacetylene		×	×			×	×	

TABLE I (continued)

Compound	800°C		850°C		900°C		950°C	
	T	GW	T	GW	T	GW	T	GW
Dihydroanthracene	x	x	x	x	x	x	x	x
Dihydrophenanthrene			x					
2-Methylfluorene	x				x			
1-Methylfluorene		x		x		x	x	x
Unknown, MW 206	x	x				x		
Unknown, MW 192		x	x			x		
(p-Methylphenyl)phenylacetylene	x	x	x	x	x	x	x	x
Phenanthrene	x	x	x	x	x	x	x	x
Unknown, MW 192						x		
Unknown, MW 206	x	*	x			x		
1-Phenylnaphthylene	x	x	x	x	x	x	x	x
3-Methylphenanthrene	x	x	x	x	x	x		
o-Terphenyl	x	x	x	x	x	x		
Unknown, MW 204		x						
2-Methylantracene		x	x					
9-Methylphenanthrene	x			x	x	x		
4,5-Methylenephenanthrene						x		
Tetrahydropyrene	x	x	x	x	x	x		
Dihydropyrene (MW 204)		x						
2-Phenylnaphthylene	x	x	x	x	x	x	x	x
1-Benzyl-naphthylene (MW 218)		x				x		
Unknown, MW 204		x				x		
Unknown, MW 204		x				x		
Fluoranthene		x	x		x	x	x	x
Diphenylacetylene	x	x	x	x		x		
2-Benzyl-naphthylene (MW 218)		x	x			x		
Pyrene		x			x	x	x	x
Unknown, MW 218		x						
m-Terphenyl	x	x	x	x	x	x		x
p-Terphenyl		x	x					
Benzo[a]fluorene	x	x	x	x	x	x		x
Benzo[b]fluorene	x	x	x	x	x	x	x	x
Unknown, MW 228						x		
Unknown, MW 242		x						
5,12-Dihydronaphthacene		x				x		
Diphenylindene (?)	x	x						
Benzo[c]phenanthrene		x	x		x	x		x
Benzo[a]anthracene		x	x					
Chrysene	x	x	x	x	x	x	x	x
1,2'-Binaphthyl	x	x	x	x	x	x	x	
11-Methylbenzo[a]anthracene		x						
Unknown, MW 280		*	x		x			

(Continued on p. 208)

TABLE I (continued)

Compound	800°C		850°C		900°C		950°C	
	T	-GW	T	GW	T	GW	T	GW
Diphenylindene (?)			×					
1-Phenylphenanthrene	×	×	×	×	×	×	×	×
Unknown, MW 280		×			×	×		
2,2'-Binaphthyl				×		×		×
Unknown, MW 278		×				*		
Benzo[<i>j,k</i>]fluoranthene			×		×		×	
Benzo[<i>e</i>]pyrene		×						×
3-Methylcholanthrene						×	×	×
Quaterphenyl	×	×		×				
Diphenylacenaphthylene (MW 304)							×	
Picene		×				×		
Benzo[<i>ghi</i>]perylene								×

* Multiple isomers detected.

(2 isomers), diphenylacetylene, diphenylmethane, and 1,3-diphenylpropane. These constitute the early-eluting compounds, with retention times less than phenanthrene. Also in this region were several compounds whose identities could not be determined conclusively by mass spectral data. Three compounds of molecular weight 192 were found with retention indices which did not correspond to known compounds. Possible compounds of molecular weight 192 are C₁₅H₁₂ isomers, such as (methylphenyl)phenylacetylenes and dibenzocycloheptene isomers. In addition to compounds of molecular weight 192, there are also isomers of molecular weight 194 present. These isomers may be diphenyl propanes, (methylphenyl)phenylethylenes, and dimethyl- or ethylfluorenes. All three of the unknown 194 compounds eluted in the region following the diphenylethylenes. The two diphenylethylene isomers were identified on the basis of boiling points and mass spectra; while it is felt that the identifications are correct, compounds such as (*p*-methylphenyl)phenylethylene and 1-phenylindene cannot be ruled out as possibilities. The unknown 194 compounds are not dimethyl or ethyl fluorenes from retention behavior, and must be assumed to be other (methylphenyl)phenyl acetylene isomers or diphenyl propanes.

Upon increasing the temperature to 950°C, many of the substituted aromatics are no longer formed. For example, 1- and 2-methylnaphthalene are no longer identified by GC-MS at the higher temperature. 2- and 3-methylbiphenyl have also disappeared, along with 1,3-diphenylpropane, diphenylacetylene, 3- and 9-methylphenanthrene, *o*-terphenyl, and many of the molecular weight 192, 194, 204 and 218 isomers which were unidentified. From comparison of the total ion chromatogram at 950°C (Fig. 4) with Fig. 3, it may be seen that the baseline in the region after 25 minutes has fewer small fluctuations at 950 than at 800°C. These small fluctuations are components which are difficult to identify due to poor spectra. It appears that more chrysene (retention time 28 min) and benzo[*e*]pyrene (retention time 34 min) are formed at the higher temperature. The major component identified in the 950°C sample is phenanthrene, with biphenyl as the second most abundant species by MS.

Naphthalene is present in smaller quantities, along with the methylfluorenes, fluorene, methylbiphenyl, and other components eluting in the early portion of the chromatogram. The list of compounds identified in the polystyrene samples is given in Table I.

CONCLUSIONS

Combustion of polystyrene appears to be a significant source of polycyclic aromatic hydrocarbons, especially at lower temperatures. Table II lists the total amount (mg) of various PAHs identified in the cold trap combustion effluents. It appears that the greatest total amounts of the compounds listed occurs at 900°C, with a significant decrease in PAH production upon changing from 900 to 950°C.

Complete combustion does not appear to be achieved. The large amounts of PAH produced support the observations of Morikawa²³ and Pasternak *et al.*²⁴, namely, that large quantities of PAHs and soot are produced during polystyrene combustion. It is interesting to note that the majority of PAHs appears to be associated with the particulate matter. Most of the particulate matter will be retained on the glass wool filter and the PAHs are found mostly in this filter as is seen from Table II.

TABLE II

TOTAL AMOUNTS (mg) OF VARIOUS PAHs IDENTIFIED IN POLYSTYRENE COMBUSTION

Cold traps only.

Compound	800°C	850°C	900°C	950°C
Indene	15.83	13.58	11.34	3.715
Naphthalene	20.91	21.66	26.94	17.49
2-Methylnaphthalene	1.166	0.839	1.134	0.440
1-Methylnaphthalene	1.200	1.163	1.075	0.408
Biphenyl	4.115	5.009	7.456	7.158
Acenaphthylene	1.734	1.405	0.714	1.264
4-Methylbiphenyl	0	0.847	0.587	0.409
Fluorene	2.735	3.434	3.199	1.726
9-Methylfluorene	0.746	2.696	2.102	0.756
Dihydroanthracene	2.554	0	1.419	0
<i>p</i> -Methylphenylphenylacetylene	2.492	2.453	1.513	0.298
Phenanthrene	12.58	16.14	15.38	9.145
1-Phenylnaphthalene	5.548	4.188	4.354	1.270
<i>o</i> -Terphenyl	0.805	0.704	0.622	0
2-Phenylnaphthalene	10.08	10.26	8.190	2.243
Fluoranthene	0.693	0.840	0.938	0.911
Pyrene	0.873	0.579	0.649	0.500
<i>m</i> -Terphenyl	1.265	0.907	0.773	0
Benzo[<i>a</i>]fluorene	1.281	1.196	1.089	0.444
Benzo[<i>c</i>]phenanthrene	0.567	0.409	0.421	0
Chrysene	0.710	0.796	0.978	0.532
1-Phenylphenanthrene	0.137	0	0	0
Total amount	87.961	89.187	90.873	48.709
Total PAHs (approx.)	706	476	344	83.2

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