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PYROLYSIS STUDIES ON POLYALKYLENE PHTHALATES

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Abstract—The synthesis and identification of pyrolysis products of five polyalkylene phthalates are reported. The pyrolysis products are separated in a capillary gas chromatograph and the products are identified using a mass selective detector. The major degradation products for the polyesters now investigated are phthalic anhydride and the appropriate diol. In nearly all the polyesters studied, cyclic ether from the diol and the cyclic diester formed from phthalic anhydride and the diol are detected. A wide variety of low molecular weight compounds and considerable quantities of complex mono- and diesters of phthalic acid are identified among the pyrolysis products. The mode of formation of the products identified by GC/MS analysis are discussed with reference to the general polyester degradation mechanism.

INTRODUCTION

Phthalic anhydride is one of the main components in the synthesis of general purpose unsaturated polyester resins [1], which find wide applications. Of the several methods employed for the modification of these resin systems, one is to change the diol component. The degradation behaviour of various polyesters has been reviewed [2]. In the case of polyesters with aliphatic diols, no systematic study dealing with the dependence of the degradation behaviour on the diol component has been reported. In order to understand in detail the mechanistic aspects of thermal degradation of the polyesters in general, several polyalkylene phthalates were chosen as model compounds in the present investigation and were synthesized and studied. All the pyrolyses were carried out in vacuum and a low pyrolysis temperature was chosen to avoid secondary reactions of the primary pyrolysis products. Taking into account the general polyester degradation mechanism, the possible routes for the formation of products are deduced and discussed.

EXPERIMENTAL

Materials

Phthalic anhydride, 1,2-ethanediol, 1,3-propanediol, 1,5-pentanediol and 1,6-hexanediol were supplied by Merck (Darmstadt, West Germany). 1,4-Butanediol was obtained from Loba Feinchemie (Fischamend, Austria). The other chemicals and solvents were from Merck and were used without further purification.

Synthesis of polyesters

All the polyesters containing phthalic anhydride and one of the above mentioned diol as the monomers (mole ratios 1.0:1.1) were synthesized by melt condensation in vacuum. Typically the monomers were fed into the reaction flask and the system was pumped down to a pressure of 100 Pa (1 mb) at room temperature (20°C). Then the temperature was slowly increased to 50°C within a period of 1 hr and to 100°C within a further period of 1 hr. Then the temperature of the melt was slowly increased to 150°C over 2 hr and the condensation reaction was allowed to proceed at this temperature for a further period of 2 hr. Finally the temperature of the molten polymer was increased to 180–190°C over a period of 2 hr and subsequently the pressure of the system was also reduced to 50 Pa (0.5 mb). At this stage the polymerization was allowed to proceed for 3 hr.

The polymer melt was then allowed to reach room temperature and then brought to atmospheric pressure. The materials thus obtained were finally dried *in vacuo* 1000 Pa (10 mb) at 100°C for 5 hr and stored in a refrigerator (0°C) for further study. Table 1 gives a summary of the samples and the abbreviation code; the acid numbers obtained by the particular procedure of synthesis are also listed. Note that the acid number depends whether the diol component has either an even or odd number of carbon atoms. Therefore for polyesters P122, P144 and P166, a post-condensation was performed utilizing azeotropic condensation technique with toluene until the acid number reached a value below 60 mg KOH/g polyester. The acid numbers for these polyesters are presented in Table 1.

METHODS

Pyrolysis in vacuum

The pyrolysis apparatus is detailed elsewhere [3]. In principle a pyrolysis tube attached to a U-shaped

Table 1. Samples synthesized and codes of abbreviation

Diol component	Resulting polymer	Sample code	Acid number (mg KOH/g)
1,2-Ethanediol	Poly(oxyethyleneoxyphthaloyl)	P122	43.3 (174.2)
1,3-Propanediol	Poly(oxytrimethyleneoxyphthaloyl)	P133	9.1
1,4-Butanediol	Poly(oxytetramethyleneoxyphthaloyl)	P144	58.5 (177.3)
1,5-Pentanediol	Poly(oxypentamethyleneoxyphthaloyl)	P155	47.4
1,6-Hexanediol	Poly(oxyhexamethyleneoxyphthaloyl)	P166	16.7 (177.6)

The values in parentheses refer to the acid number for the non-post-condensed samples.

cooling trap for sampling, which could be cooled in liquid N_2, was employed. The cooling trap was connected via stopcocks and a safety trap to a rotary pump. As in thermal volatilization analysis (TVA) [4], it was possible to monitor pressure changes during degradation. The pyrolysis vessel was heated during the experiments by placing it in a gas chromatographic oven. About 1.0–1.5 g of the material was weighed into the pyrolysis tube and the system was evacuated to a pressure of 1 Pa (0.01 mb). During this evacuation process (30 min), the temperature of the oven was kept at 100°C in order to remove any low molecular weight volatile impurities in the sample. The material was then pyrolyzed by heating at 20°C/min from 100°C to 440°C and then kept at 440°C for 23 min. The volatile products formed during pyrolysis were allowed to condense on a frozen matrix of 0.5 ml 1,2,4-trichlorobenzene, cooled using liquid N_2. After thawing, the trichlorobenzene containing the volatile products was dried using anhydrous sodium sulphate and preserved for analysis. In the colder parts of the pyrolysis vessel, generally the less volatile products condense and this cold ring fraction was extracted with 2.0 ml acetone and stored for further analysis.

SEPARATION AND IDENTIFICATION OF THE PYROLYSIS PRODUCTS

The separation of the pyrolysis products was done in a Hewlett–Packard HP 5890 gas chromatograph containing a 12 m capillary column (crosslinked methyl silicone gum) and the identification was done using a HP 5970 mass selective detector. A HP 59970A workstation was used for the data analysis. The temperature program used in the GC/MS analysis for the volatiles and cold rings was: initial temperature 40°C, initial time 5.0 min, heating rate 10°C/min, final temperature 240°C, final time 5.0 min, injector temperature 250°C, detector temperature 280°C, masses scanned 20–550 amu, injection volume 1 μl and carrier gas He.

RESULTS AND DISCUSSION

Thermal volatilization traces

The thermal volatilization analysis curves obtained for the five polyesters are shown in Fig. 1. The polyesters containing even numbers of carbon atoms in the diol component (P122, P144 and P166) show a two stage degradation pattern whereas the polyesters comprising odd numbers of carbon atoms in the diol part (P133 and P155) show nearly a single stage degradation process. The maximum evolution of the volatiles in the first step of the even numbered cases is in the range of 165–185°C oven temperature and is due to release of residual toluene as proved by an on-line pyrolysis technique. Further for comparison the TVA-traces of P122, P144 and P166 of high acid numbers are also presented. Here also a two stage degradation pattern is obtained which is slightly more structured but the maximum of the first stage of degradation is shifted to 260–270°C.

GC/MS studies

In the volatile fraction, 46 compounds are identified and in the cold ring fraction 25 compounds are identified. In many cases the mass spectra evaluated by computer search fitted very well with the library documented spectra and the suggestions made by the computer were reasonable. In other cases, the suggested structures did not fit well or were unreasonable. In such cases the mass spectra were evaluated manually and because of the lack of published spectra the suggested structures are tentative.

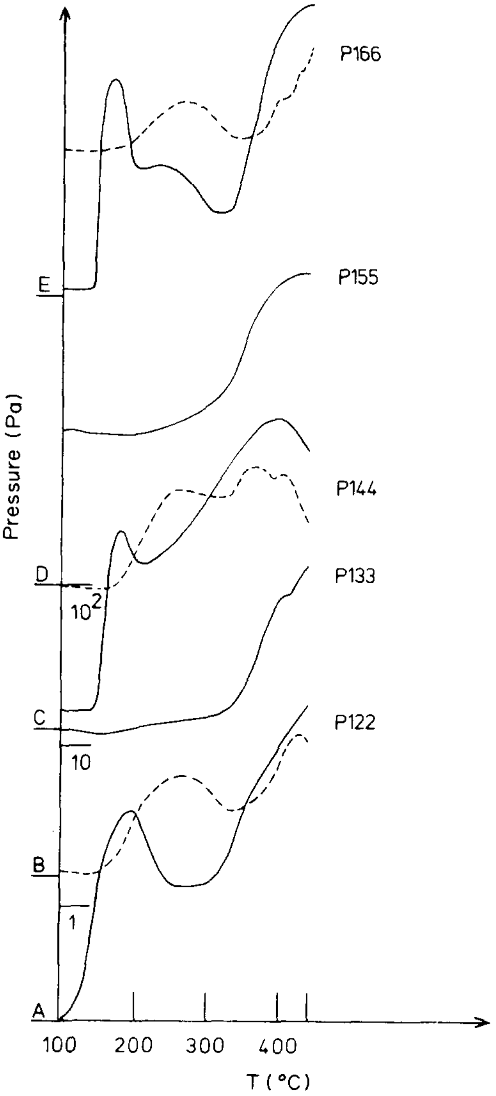


Fig. 1. TVA traces of P122, P133, P144, P155 and P166 polyesters. The curves for the samples P133, P144, P155 and P166 are shifted on the ordinate by the distances $\overline{AB}$, $\overline{AC}$, $\overline{AD}$ and $\overline{AE}$ respectively. The dashed lines refer to the samples with high acid number (cf. Table 1).

The major products of degradation identified in both the volatile and cold ring fractions are summarized in Table 2 comprehensively. The numbers in Table 2 refer to relative amounts of the particular compound identified among the pyrolysis products calculated on the basis of the total ion current (TIC%) intensities. Detailed information regarding the various compounds identified and their mass spectral fragmentation pattern is available from the authors on request.

Table 2. Vacuum pyrolysis of polyalkylene phthalates at 440°C

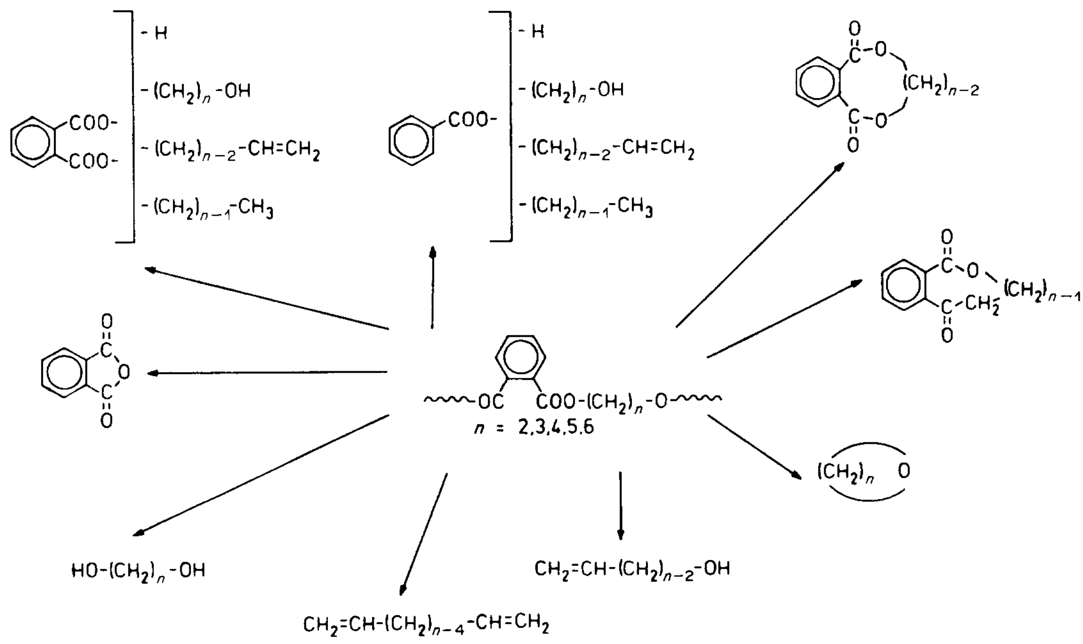
Main Products identified Compound/Compound Class	Relative total ion current intensities (TIC%)				
	P122	P133	P144	P155	P166
Volatile fraction					
Phthalic anhydride	4.4	25.7	1.5	3.8	—
HO—$(CH_2)_n$—OH	—	—	—	3.7	—
CH_2=CH—$(CH_2)_{n-4}$—CH=CH_2	—	—	1.6	3.8	8.6
CH_2=CH—$(CH_2)_{n-2}$—OH	—	18.3	10.6	49.4	68.9
Cyclic ethers or isomers	36.3	21.2	60.9	36.4	2.4
Dihydrofuran	—	—	6.1	—	—
2-Methoxytetrahydrofuran	—	—	1.2	—	—
Allylbenzoate	—	8.0	—	—	—
Sum of the major products	40.7	73.2	81.9	97.1	79.9
Sum of the minor products	59.3	26.5	18.1	2.9	20.1
Total identified products	100.0	99.7	100.0	100.0	100.0
Cold ring fraction					
Phthalic anhydride	60.0	39.4	52.4	55.4	47.8
HO—$(CH_2)_n$—OH	2.8	6.9	37.6	14.8	32.6
Cyclic diesters (**I–IV**)	2.4	5.6	2.1	4.9	—
HOOC—C_6H_4—$(CH_2)_{n-2}$—CH=CH_2	5.2	—	—	3.4	7.7
$C_{11}H_{12}O_5$ (**VIII**)	26.7	—	—	—	—
$C_{13}H_{16}O_5$ (**IX**)	—	26.4	—	—	—
Propenylethyl phthalate	—	14.4	—	—	—
Pentenylbutyl phthalate	—	—	—	20.3	—
Sum of the major products	97.1	92.7	92.1	98.8	88.1
Sum of the minor products	2.8	7.2	7.8	1.1	11.8
Total identified products	99.9	99.9	99.9	99.9	99.9

For structural details of compounds designated with roman numbers refer to Scheme 2.

From the information obtained by the identification of the degradation products, a general simple scheme of degradation can be established, see Scheme 1. Subsequently the degradation routes in the scheme are discussed and supported by the product analysis. Afterwards important exceptions and anomalies in the degradation path are mentioned.

(*A*) *Formation of diols.* In all the polyesters studied, the particular diol initially taken in the monomer feed was recovered in the cold ring fraction among the major components, i.e. 1,2-ethanediol was seen among the pyrolysis products of the polyester P122. The formation of the diol can be easily explained by a two step reaction. Homolytic cleavage at the acyl–oxygen bond in the polyester backbone followed by H·abstraction will lead to the formation of hydroxy terminated products.

$$\begin{gathered}\sim\!\!\sim\text{—OC—}C_6H_4\text{—CO—O—}(CH_2)_n\text{—O—}\sim\!\!\sim\\ \downarrow\\ .\text{O—}(CH_2)_n\text{—O—}\sim\!\!\sim\\ \downarrow\\ \text{HO—}(CH_2)_n\text{—O—}\sim\!\!\sim\end{gathered}$$



Scheme 1

$n = 2, 3, 4, 5$ and 6 $C_6H_4=$

If such a reaction proceeds further at the other end of the ester link in the hydroxy terminated products, free diols will be released from the degrading system.

(*B*) *Formation of the aliphatic unsaturated alcohols.* The formation of unsaturated alcohols, which are also among the major products of degradation, can be imagined in various ways. It is possible that the diols primarily formed may undergo dehydration yielding the unsaturated alcohols,

$$HO{-}(CH_2)_n{-}OH - - H_2O \rightarrow CH_2{=}CH{-}(CH_2)_{n-2}{-}OH$$

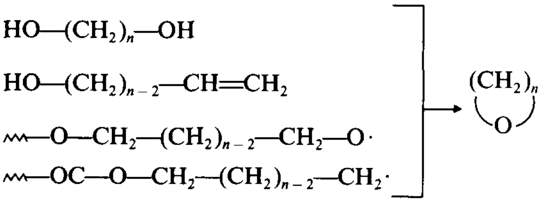
or they can be formed directly by a β-scission followed by a CO–O bond homolysis and H· abstraction at the other end of the ester link.

$$\begin{array}{c} \sim\!\sim{-}OC{-}C_6H_4{-}CO{-}O{-}(CH_2)_n{-}O{-}\sim\!\sim \\ \downarrow \beta\text{-scission} \\ CH_2{=}CH{-}(CH_2)_{n-2}{-}O{-}\sim\!\sim \\ \downarrow CO{-}O \text{ homolysis and } +H\cdot \\ CH_2{=}CH{-}(CH_2)_{n-2}{-}OH \end{array}$$

In the case of P122, the vinyl alcohol initially formed of course will be recovered as acetaldehyde which was indeed detected among the pyrolysis products. Further allyl alcohol (P133), 3-butene-1-ol (P144), 4-pentene-1-ol (P155) and hexenol (P166) were detected.

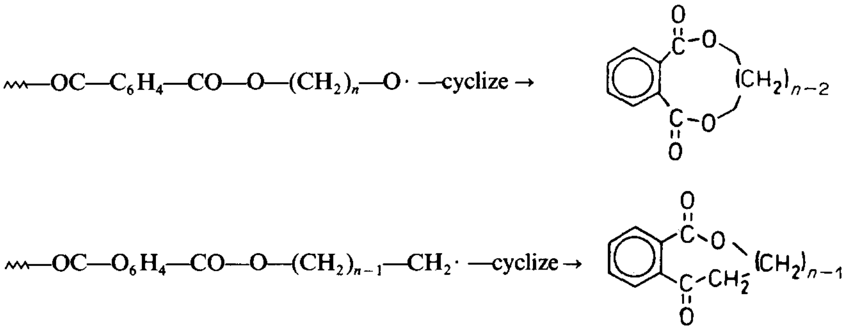
(*C*) *Formation of dienes.* By a similar mechanism, dienes with double bonds at both the ends of the alcohol part are formed. For example 1,3-butadiene, 1,4-pentadiene and 1,5-hexadiene were identified. It is interesting to note that 1,5-hexadiene is not only formed from P166 (8.6%) but also during the degradation of P133 (6.7%) and P155 (0.2%). In the latter cases, hexadiene may be formed by the subsequent recombination of propenyl radicals. Besides these dienes, 1,4-hexadiene and 1,3,5-hexatriene were also detected in the pyrolysis products. The formation of these compounds can be explained by isomerization and dehydrogenation of the diene initially formed. Further, 1-hexene was detected for P166. Its formation can be easily visualized either by hydrogenation of the diene formed or by an alkyl-oxygen cleavage in the unsaturated units formed followed by H· addition.

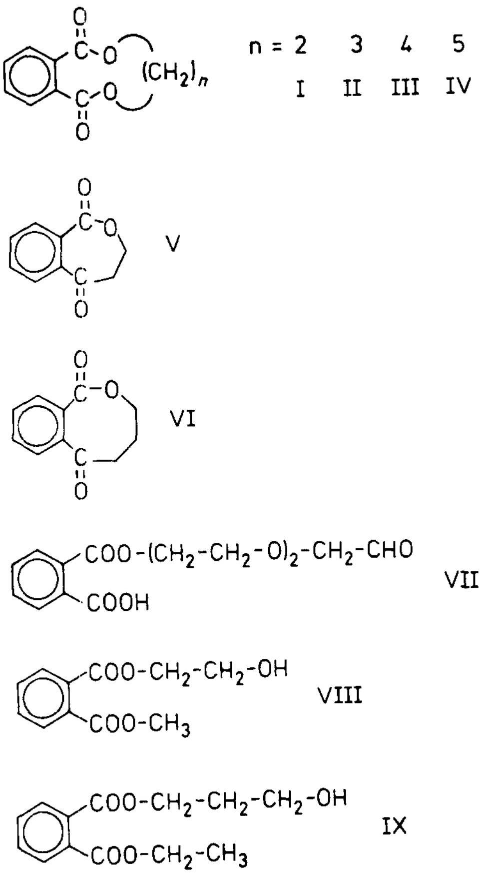
(*D*) *Formation of cyclic ethers.* Except the P122 and P133 polyesters, all the other polyesters studied showed the formation of cyclic ethers (tetrahydrofuran, dihydrofuran, tetrahydropyran and oxepan) in the pyrolysis experiments. Several possible routes are detailed below. (i) The diols produced can undergo cyclodehydration. (ii) The aliphatic olefinic alcohols formed may take part in an intramolecular addition reaction. (iii) The alkoxy radicals formed during the main chain scission can undergo cyclization. (iv) The alkyl radicals formed may cyclize during degradation.



The fact that tetrahydrofuran is detected not only for P144 but also for P155 (0.1%) suggests that alkyl radicals are not formed exclusively by scission of a carbon–oxygen linkage but also by carbon–carbon scission (assuming a radical mechanism). For P122, instead of oxirane, acetaldehyde is formed which is also seen for P133. This may be taken as an isomerization product of oxirane or acetaldehyde may be formed by some special mechanism [3]. For P133, it is doubtful whether the product in question is oxetane or 2-propenal. The formation of cyclic ethers is a major reaction during degradation and is in particular favoured for P144 and P155 indicating the tendency for information of 5- and 6-membered rings.

(*E*) *Compounds containing aromatic units.* These particular compounds derived from the phthalate moiety include phthalic anhydride as the most prominent compound and further miscellaneous esters of either phthalic or benzoic acid. The formation mechanism of phthalic anhydride is well established [5]. The various possibilities for ester formation are shown in Scheme 1. The scheme shows that various combinations of hydroxy terminated, olefinic terminated and alkyl terminated diesters and similarly terminated monoesters of phthalic acid can be formed. The same holds for the benzoate esters. Further, cyclic diesters of phthalic acid and keto-lactones are formed.





Scheme 2

Formally the latter compounds can be explained by attack of an alkyl radical linked to a phthalic unit intramolecularly to the carbon atom of the other acyl unit. The number of carbon atoms in particular, in the case of alkyl terminated esters, does not necessarily reflect the number of carbon atoms originally present in the diol component. In Table 2 and in Schemes 1 and 2, many compounds are given to illustrate the foregoing general discussion.

(*F*) *Miscellaneous compounds*. Explanation of some of these compounds is rather difficult, at least because in the case of isomers the true position of the functionalities is not exactly known. Three isomers of hexenal and two of cyclohexenol were identified for the P166 polyester. 2-Methyl-1,3-dioxolane is seen among the degradation products of P122. It is formed by a secondary reaction between 1,2-ethanediol and acetaldehyde [3]. 3-Methylcyclopentene detected for P133 may be formed by the isomerization of the hexadienes. 2-Methoxytetrahydrofuran and 2-methyltetrahydropyran formed from P144 and P155 respectively can be explained by the addition of methoxy- or methyl radicals formed by some chain scission reactions to the cyclic ether radical intermediates. Benzene and toluene were formed by ejection of carbon dioxide from benzoic acid esters and subsequent degradation of alkyl- or alkenyl- or hydroxyalkylbenzenes.

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