

Thermal Degradation of Polyester Thermosets Prepared Using Dibromoneopentyl Glycol

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Synopsis

Polyester thermosets have been prepared from maleic anhydride, phthalic anhydride, dibromoneopentyl glycol, and styrene, and their thermal degradation has been studied. Thermogravimetry has shown that degradation in air occurs in three main stages. For the 10% bromine polyester, the weight losses corresponded to 16.3%, 69.7%, and 13.9% of the original polymer weight—the temperatures of the DTG peak maxima being 217°C, 345°C, and 530°C, respectively. Infrared analysis of the residues showed that above 250°C there was a gradual reduction in the absorbance of all peaks with increasing temperature, indicating the degradation of all parts of the 3-dimensional polymer structure was occurring in a simultaneous manner. Degradation of the dibromoneopentyl glycol polyesters at 530°C in air proved to be a very complex process since a mixture of organic products was produced which gave rise to well over 100 peaks in the capillary column chromatograms. Under the conditions used, the low temperature degradation products proved to be rich in phthalic anhydride with no benzaldehyde being detected. The yields of benzene, toluene, styrene, and naphthalene increased with increase in temperature.

INTRODUCTION

Polyester thermosets have been produced commercially for about three decades. Since 1960 they have experienced a considerable growth rate and are predicted to do so in the foreseeable future. They are used extensively in the marine market for pleasure boats, in automobile parts where the strength-weight ratio is important, in the construction industry for various types of panels, and in numerous ducting and electrical applications.

These thermosets, which are usually reinforced by glass fibers, are prepared by crosslinking a low molecular weight polyester with styrene. The polyesters are prepared using three types of monomers—unsaturated acids, saturated acids, and glycols. In general purpose grades, these components are often maleic anhydride, phthalic anhydride, and propylene glycol. Although a wide variety of performance specifications can be satisfied by varying the proportions of these basic ingredients, different monomers can be used where particular characteristics are desired.¹⁻³ In particular, isophthalic acid gives improved resistance to hydrolysis and better mechanical properties whereas tetrabromophthalic anhydride increases flame resistance. The diversity of final formulations obtainable is further increased by the addition of additives to the low molecular weight polyesters prior to curing with styrene. In this way the residual surface tack of the cured polyester can be reduced, its weathering properties improved, and its flame resistance further increased.

Despite their wide usage, no clear picture has emerged from previous studies

of their thermal and thermooxidative degradations. This is a direct result of the somewhat limited number of investigations that have been carried out, the specific aims of some of the research programs, and the large number of polyester formulations that have been used. Besides the standard polyesters,⁴⁻¹⁵ investigations have involved polyesters crosslinked with methyl methacrylate¹⁶ and those made from isophthalic acid,¹⁷ succinic anhydride,¹⁸ adipic acid,¹⁹ and various halogen-containing monomers.²⁰⁻²⁵

The most comprehensive studies of the degradation of the standard polyester thermosets have been performed by Anderson and Freeman⁴ and Moore and co-workers.⁵⁻⁷ The work involved thermogravimetry and differential thermal analysis studies of the polyesters, examination of the thermally degraded resins by infrared spectroscopy, and a limited attempt at identification of the volatile degradation products through collection and analysis. More recently, Marshall¹³ used pyrolysis in the inlet of a mass spectrometer as a means of characterizing the polyesters. Although useful for studying their thermal degradation, this technique does not yield any information regarding the thermooxidative degradation of the polyesters, the area of most interest to us.

Luce and co-workers¹⁷ developed a method based on pyrolysis-gas liquid chromatography for characterizing polyesters used in cured laminates. The method allowed the polyester composition to be fingerprinted, but no extensive identification program of the volatiles emitted was undertaken. Using this technique, Belinski and co-workers¹⁸ and Vijayakumar and Fink²⁵ have identified a number of the volatile products from polyesters based on succinic and chloroendic anhydrides, respectively. The complexity of the pyrolysate from polyesters is well shown by the need for Green, Hume, and Kumar²⁴ to use three chromatographic columns when trying to correlate the yield of volatile aromatic products with smoke formation.

The object of this work was to obtain a better understanding of the mode of thermal degradation of the brominated polyester thermosets. The bromine was incorporated into the polyester using dibromoneopentyl glycol—one of the reactive flame retardant components used in the industry.²⁶

EXPERIMENTAL

Preparation of the Polyester Thermosets

The resins used in this investigation were prepared from phthalic anhydride (BDH), maleic anhydride (Hopkins and Williams), and neopentyl glycol (Aldrich Chemical) or dibromoneopentyl glycol (Dow Chemical) using a 1:1:2.2 mole ratio. The level of bromine in the final polymer formulation was varied by blending polyesters made from dibromoneopentyl glycol (DBNPG) and neopentyl glycol (NPG) after the bromine concentration in the DBNPG resin had been determined by oxygen flask combustion followed by potentiometric titration with silver nitrate. Curing of the low molecular weight polyester was carried out using styrene (BDH) as the crosslinking monomer. Details of a typical polymerization and curing procedure have been described elsewhere.²⁷

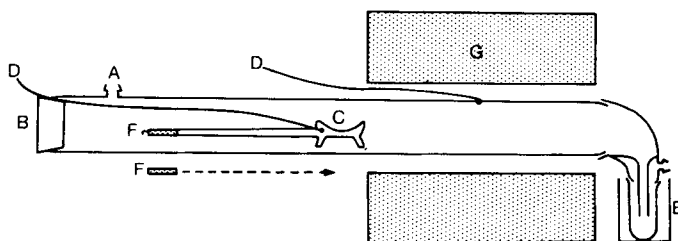


Fig. 1. Furnace-trapping system: (A) gas inlet; (B) cork bung; (C) sample boat; (D) thermocouples; (E) cardice-acetone trap; (F) magnet and sample entry system; (G) furnace.

Thermogravimetry

Thermogravimetry was performed on a Stanton Redcroft TG 770 Thermo-balance using 10-mg samples heated in flowing air or nitrogen. Generally, a heating rate of $10^{\circ}\text{C min}^{-1}$ was used, although the heating rate was shown to have little effect on the mode of decomposition. The DTG curves were obtained electronically. The reproducibility of the mass losses was within $\pm 1\%$ and of temperature events $\pm 5^{\circ}\text{C}$.

Thermal Degradation

Thermal degradation of the polyester thermosets, to produce volatile decomposition products for examination, was carried out by two methods. Initially, a Curie point pyrolyzer-gas chromatograph system was used for degradation in nitrogen but later a furnace trapping-gas chromatograph system was developed for studies in both air and nitrogen atmospheres.

Curie Point Pyrolysis. The Pye Curie point pyrolyzer was used in conjunction with a Pye 104 Gas Chromatograph. Optimum sample size was found to be 100–150 μg , the pyrolysis being carried out by keeping the sample at the appropriate temperature for 10 s. The sample was held on the pyrolysis wire by flattening the last 10 mm of a clean, preweighed wire in a vice, bending the flattened end around the sample and crimping it in. Chromatography columns (1.5 m \times 6 mm i.d.) of Poropak Q, for the very volatile components, and Carbowax 20 M were used for the separation of the degradation products. Identification of the latter was attempted using the Pye 104 Gas Chromatograph attached to an A.E.I. MS30 mass spectrometer using helium as the carrier gas and recording the spectra at an electron beam energy of 70 eV.

Degradations Using a Furnace Trapping System. The products from all stages of thermal degradation in air were investigated using a furnace trapping system (Fig. 1). The apparatus consisted of a one metre silica tube (i.d. 20 mm) passing through a Beckman tube furnace. The temperature stability of the furnace was such that an additional controller was necessary to ensure accurate control to within 3°C . Additional Pt-13% Rh thermocouples were used to monitor the sample and furnace temperature, these being connected to a Comark digital thermometer.

When using the furnace to investigate the organic degradation products, a small silica sample boat was used which had a hook at one end to enable it to be entered or withdrawn from the furnace. A 10 cm^3 tapered B10 test tube was used

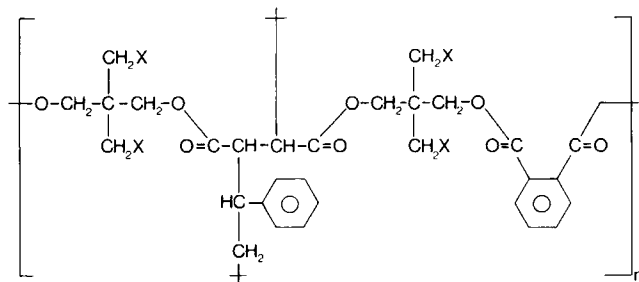


Fig. 2. Structure of the polyester thermoset.

to collect the volatiles in the cardice-acetone cold trap. The gas flow rates were kept in the region of 3–6 cm³/min so as not to evaporate the volatiles once condensed. The pyrolysis experiments were carried out by placing the preweighed sample boat, containing ~200 mg of the polyester samples (72–100 mesh), into the furnace for 15 min. After this period the sample boat was removed from the furnace to the cooler side of the silica tube so that volatiles still evolving from the sample were swept through into the cold trap. The residue and volatiles were weighed and any small amount of condensed volatiles remaining in the tube were washed through into the collection tube using diethyl ether. In this way all the volatile organic degradation products were obtained as a solution in diethyl ether. The resulting solutions were analyzed on a Perkin-Elmer Sigma 3B Gas Chromatograph using a 25-m OV 101 fused silica capillary column and appropriate temperature programming. A Spectra-Physics Autolab Minigrator was used to obtain retention times in seconds and peak areas of the components in arbitrary units. Under the conditions used, the reproducibility of the areas was in the range of 5–15% and for retention times better than 1%. Response factors for each of the components were not determined. Consequently, only the relative amounts of the degradation products could be compared between samples. A computer program was written to convert the peak area information into a table of percent abundance of each unidentified breakdown product. Using it, any number of peaks above a specific level could be resolved to 100%, and any one peak could be ratioed to all the others. All the chromatographic results were determined at least in triplicate and rogue values rejected before they were averaged. The results quoted and plotted are the average of such determinations.

Samples of the partially degraded polyester formulations were studied by infrared spectroscopy using the procedure reported elsewhere.²¹ Sublimates were studied as nujol mulls,²⁰ and identification of the furnace degradation products was attempted using a V.G. Micromass ZAB-2F Mass Spectrometer.

RESULTS AND DISCUSSION

Polyester Structure. A schematic diagram of the 3-dimensional polyester thermoset, made by crosslinking the low molecular weight polyester chains with styrene, is shown in Figure 2. The letter "X" in this structure represents either a hydrogen or bromine atom depending on whether the low molecular weight polyester was made from NPG or DBNPG, respectively.

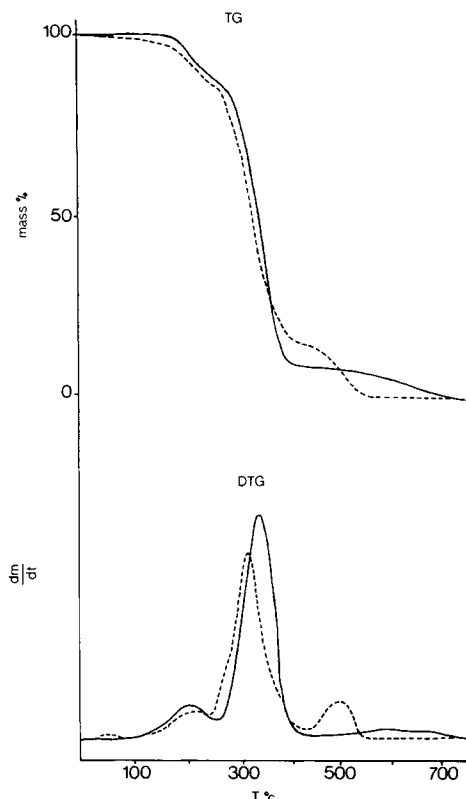


Fig. 3. Thermogravimetric curves for the 10% bromine containing polyester thermoset in air and nitrogen. Sample mass, 10 mg; heating rate, 10°C/min; air flow, 6 cm³/min. (—) 10% Br in nitrogen; (---) 10% Br in air.

Thermogravimetric Studies of the Crosslinked Polyesters. The polyester thermosets containing 5%, 10%, and 20% bromine were observed to undergo thermal degradation in air in three stages.²⁰ For the 10% bromine polyester, the weight losses corresponded to 16.3%, 69.7%, and 13.9% of the original polymer weight—the temperatures of the DTG peak maxima being 217°C, 345°C, and 530°C, respectively. These values did not vary to any significant extent as the bromine concentration in the polymer was varied between 5% and 20%. The thermogravimetric curve for the NPG polyester (no bromine present) was slightly different from the DBNPG curves in that the first two degradation steps overlapped considerably. Apart from this, they were similar in that these two steps still accounted for 86.6% of the total weight loss with the remainder being lost in the third step. The overall degradation pattern was very similar to that found with similar polyester thermosets,^{6,10,15} except that Anderson and Freeman⁴ had observed four stages of degradation, the second stage here being seen by them as two extensively overlapping reactions.

The infrared spectrum of the air sublimate at 200°C of the DBNPG polyesters showed that the first degradation stage corresponded mainly to evolution of phthalic anhydride while comparisons of the air and nitrogen degradations indicated that the third degradation step in air corresponded to char oxidation.²⁰ This is illustrated in Figure 3 for the 10% bromine containing polyester which

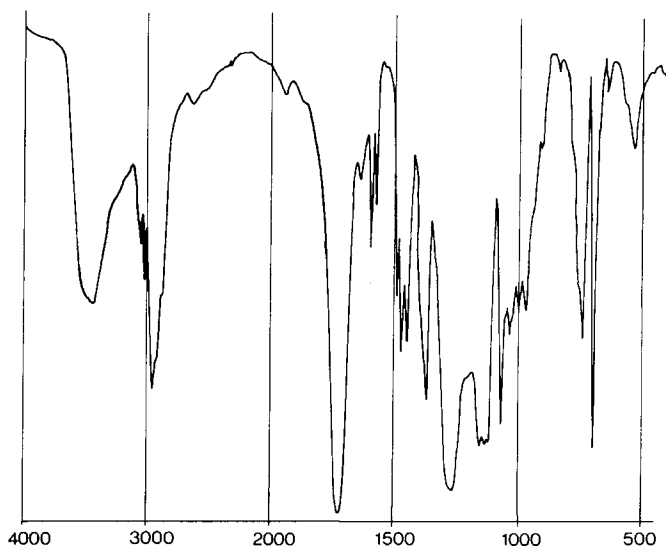


Fig. 4. The infrared spectrum of the polyester thermoset made from neopentyl glycol (NPG).

also shows that the main degradation step occurs at a lower temperature in air than it does in nitrogen. In a nitrogen atmosphere, 92.5% of the weight loss occurs in two steps before 400°C. The residue is lost gradually over a temperature range of 350°C. This slow weight loss is assumed to be due to a gradual distillation of high-boiling point materials from the tar produced.

Infrared Analysis of the Polyester Residues. The infrared spectrum of the polyester thermoset made from NPG is given in Figure 4. The spectra of the solid residues obtained by heating this polyester in air to various temperatures are given in Figure 5. Only relatively minor changes occur in the spectra as the temperature is increased. Even at 400°C, all the bands observed at room temperature are still present, although their relative intensities have changed. As was observed with the DBNPG-based polyester containing 10% bromine,²¹ the only significant additional peak first appears at around 300°C as a shoulder at 1780 cm^{-1} on the carbonyl peak. A similar peak is seen in the spectra of residues obtained by heating polyesters made from maleic anhydride, phthalic anhydride, propylene glycol, and styrene.^{7,14} Das¹⁴ assigned it to the carbonyl band of an anhydride since it was accompanied by another band at 1850 cm^{-1} . This latter conclusion is certainly feasible as there was some evidence for this second band in the spectra obtained by us and Moore and co-workers.⁷ This would tend to indicate that the bands observed at 1780 and 1850 cm^{-1} in the infrared spectra of the degradation residues in our studies might arise from anhydride units in the polyester chain. These bands fall well within the regions of the symmetric and asymmetric stretching frequencies of the carbonyl groups of anhydrides which could be expected as degradation products of the polyester.

There was some indication in the 700–800 cm^{-1} region of the infrared spectra of the bromine-containing polymers that the disubstituted aromatic ring is lost before the monosubstituted structure. Apart from these minor changes, a relative reduction in the absorbance of the residues from both the NPG and DBNPG polymers at the increased temperatures indicated that the polymers degrade so that individual monomers are given off in simultaneous fashion.

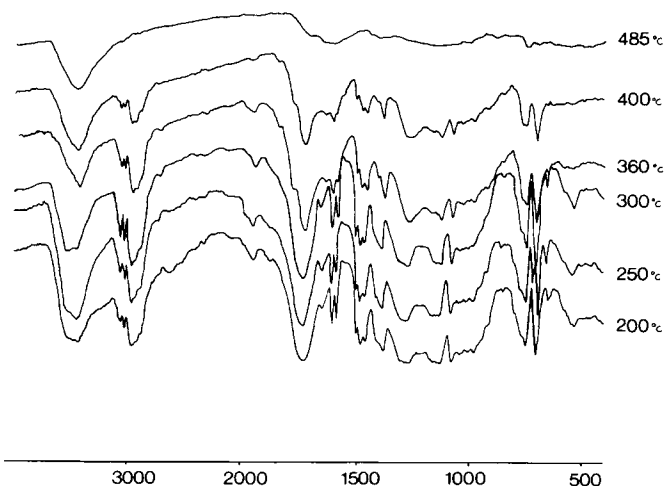


Fig. 5. Infrared spectra of the NPG polyester as a function of temperature.

Further evidence for this mode of degradation came from elemental analysis of the DBNPG polymer residues when it was observed that bromine was lost steadily throughout the whole of the degradation process.²¹ A progressive reduction in the intensity of the bands in the infrared spectra of polyesters with increase in time of heating and temperature has also been reported by Moore, Shah, and Sheldon.⁷

Curie Point Pyrolysis of the Polyesters. The initial study of the organic volatiles produced by degradation of the 20% bromine DBNPG polyesters in nitrogen was carried out using a Curie point pyrolyzer attached to a Pye 104 Gas Chromatograph. So that all the polyester would be degraded, a pyrolysis temperature of 770°C was used. Due to the wide range of breakdown products obtained, columns of Poropak Q and Carbowax 20M were both used in the attempted analysis. This approach had been originally suggested by Green, Hume, and Kumar²⁴ when studying the formation of volatile polyester degradation products. Identification of the peaks by mass spectrometry proved difficult, as a result of the small samples needed in the pyrolyzer unit. Consequently, the apparatus had to be used at high sensitivity, which emphasized the background noise of the spectra and increased the number of peaks resulting from column bleeding. These factors affected the overall reproducibility of the system. The interpretation of the spectra obtained proved to be impossible for separations on the Poropak Q column and difficult for those on the Carbowax 20M column. Only the largest of the peaks could be identified in the chromatograms from the latter, and were found to result from benzene, toluene, ethylbenzene, and styrene.

Due to the lack of reproducibility, difficulty in obtaining adequate mass spectra, and the fact that the Curie point pyrolyzer degradations could only be carried out in a nitrogen atmosphere, a furnace trapping gas chromatographic system was developed. This enabled degradation to be carried out on larger samples using an atmosphere of air or nitrogen. The lack of reproducibility of chromatograms obtained from pyrolysis experiments has also been observed by others. Green et al.²⁴ reported the coefficients of variation to be in the general range of 2–12% but as high as 10–20% for certain flame-retarded polyester for-

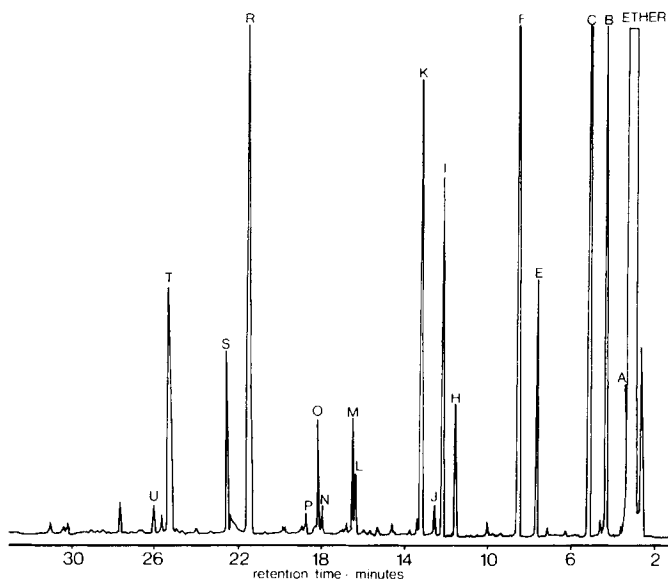


Fig. 6. Chromatogram of the degradation products obtained from the 20% bromine polyester heated to 530°C.

mulations. Similarly, May and co-workers²⁸ reported coefficients of variation of 0.9–12% in a study of the pyrolysis of paint samples, which changed to 5.5–32.9% when a drifting baseline was involved.

Analysis of the Volatiles Produced by Degradation of the Polyester in the Furnace. Degradations in air were carried out using the furnace-trapping system illustrated in Figure 1. The large sample size (~200 mg) employed during these experiments and the large volume of the combustion tube would assist the propagation of secondary reactions as would be the case in a real fire situation. The use of a capillary OV 101 column for the analysis of the volatiles enabled separation of the majority of the degradation products in a single run and eliminated the need for several columns. Degradation of the 20% bromine DBNPG polyesters at 530°C in air produced a mixture of organic products which gave rise to well over a 100 peaks in the capillary column chromatogram at maximum sensitivity. At lower sensitivities, many of the peaks resulting from very minor degradation products did not appear. A typical chromatogram obtained at a relatively low sensitivity is given in Figure 6. Chromatograms were found to be so reproducible, in terms of retention time, that it was possible to overlay them and see which peaks were common to different traces. By studying the chromatograms obtained from the products formed at different temperatures, it was found that 24 peaks were nearly always present which accounted for the bulk of the products, e.g., ~85% and ~100% at temperatures of 530°C and 250°C, respectively. To simplify comparisons between samples, only the areas from these components were quantified. Mass balances on the system at temperatures of 530°C and 250°C showed that only 4.8% and 3.0% of the original samples were not recovered. These losses could be attributed to the formation of very volatile products such as carbon monoxide and methane and to the staining and charred organic products which occurred near the outlet of the combustion tube after some degradations.

TABLE I

Data for the 24 Most Common Peaks Observed in the OV 101 Capillary Column Chromatograms of the DBNPG Polyester Degradation Products

Peak	Retention time (s)	Identity	Present in polystyrene	Present in nonstyreneated polyester
A	215	2-Methyl pentane	X	✓
B	254	Butene	X	✓
C	299	Benzene	✓	✓
D	351	—	X	✓
E	450	2-Methyl-2-butene	X	✓
F	506	Toluene	✓	✓
G	630	—	✓	X
H	685	2-Methyl-1,3-butadiene	✓	✓
I	723	Ethyl benzene	✓	✓
J	744	<i>o</i> -Xylene	X	✓
K	783	Styrene	✓	X
L	972	—	✓	X
M	980	α -Methyl styrene	✓	X
N	1067	—	✓	X
O	1082	Cyclopentyl bromide	X	✓
P	1117	Substituted styrene (dimer?)	✓	X
Q	1176	—	X	✓
R	1288	Naphthalene	✓	✓
S	1345	—	✓	✓
T	1516	Phthalic anhydride	X	✓
U	1553	—	X	✓
V	1652	—	✓	X
W	1740	—	X	X
X	1918	—	✓	✓

The degradation products from polystyrene and a styrene-free uncured polyester were compared with those of the crosslinked polyester thermosets to help with the identification of the source of each product. The 24 peaks compared are indicated in Figure 6 by a letter and are listed in Table I, together with their probable identity as determined by mass spectrometry. Not all the mass spectra could be interpreted. Some peaks gave little or no molecular ion while others were found to result from mixtures. Methyl bromide was identified by its mass spectrum, but it could not be readily quantified since its peak was only partially separated from the diethyl ether peak. Contrary to what has been reported for the polyesters made from phthalic anhydride, maleic anhydride, and propylene glycol,⁴ no benzaldehyde was detected in any of the degradation product mixtures. Typical chromatograms for the 20% bromine DBNPG polyester, showing the effect of temperature upon the degradation product distribution, are shown in Figure 7. The complexity of the product mixture obtained clearly increases with increase in temperature, the most significant changes occurring from around 350°C onwards which coincides with the peak maximum for the second degradation stage on the DTG trace.

Figures 8 and 9 are graphs indicating the variation found in the amounts of the major aromatic products produced as a function of temperature. The quantities of benzene and naphthalene increase steadily with increase in temperature. The same can be said about styrene and toluene, although both products are found in highest amounts in the degradation products produced

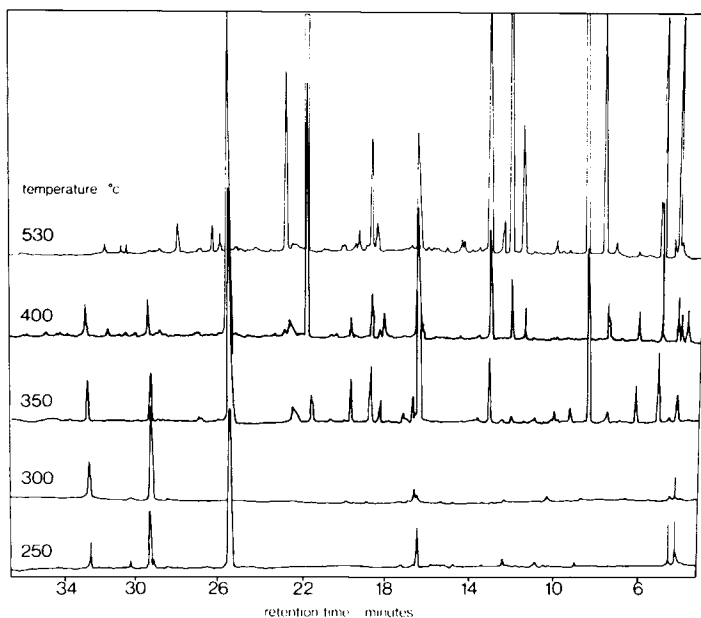


Fig. 7. Chromatograms showing the effect of temperature on the distribution of degradation products obtained from the 20% bromine polyester.

at 400°C. In contrast to this the quantities of α -methylstyrene and phthalic anhydride produced rise rapidly to reach maxima at 250°C and 300°C, respectively, and then fall sharply. At the higher temperatures further degradation of both products obviously occurs.

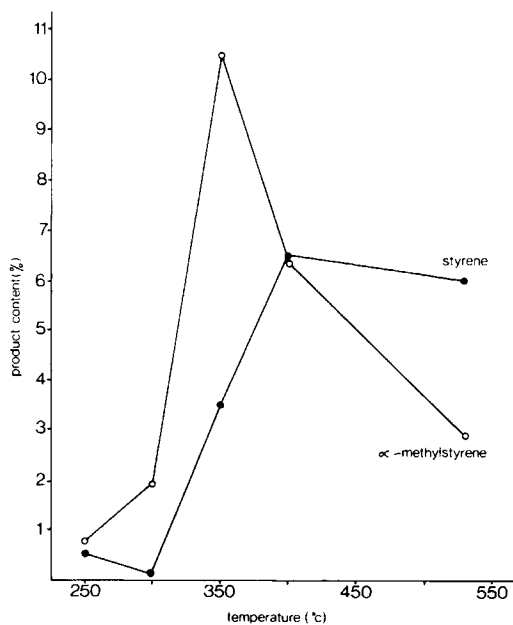


Fig. 8. The styrene and α -methylstyrene content, expressed as a percentage of the 24 most abundant degradation products, as a function of temperature.

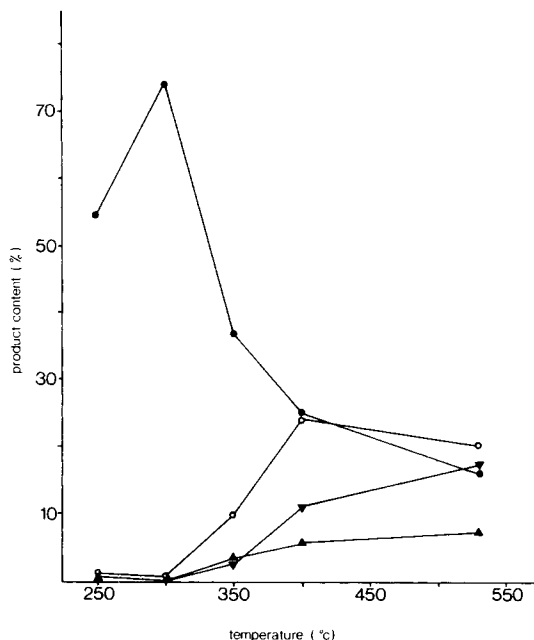


Fig. 9. The benzene (▲), toluene (○), naphthalene (▼), and phthalic anhydride (●) content, expressed as a percentage of the 24 most abundant degradation products, as a function of temperature.

In the low temperature degradations ($\leq 300^{\circ}\text{C}$) the peak due to phthalic anhydride dominated the chromatographs obtained and accounted for over 70% of the breakdown products at 300°C . Since this temperature range corresponds to the first and beginning of the second weight losses observed by thermogravimetry, it would appear that substantial breakdown of the main polyester chains occurs early on in the degradation process. This result supports our previous infrared studies²⁰ when it was shown that the sublimate at 200°C was mainly phthalic anhydride.

Thermogravimetry, as shown in Figure 3, has indicated that the main degradation stage for the DBNPG-based polyester occurs between 300°C and 400°C . In this temperature range, degradation products were observed which were characteristic of the styrene crosslinks and the remaining portions of the polyester chains. This reinforces the conclusions reached in our infrared analysis of the polyester residues when it appeared that all parts of the polyester thermoset degraded in a simultaneous fashion. At temperatures of 450 – 530°C very little change occurred in the relative amounts of the degradation products. This is only to be expected since this region corresponds to char oxidation where the major products would be water, carbon monoxide, and carbon dioxide which would not be detected by the gas chromatographic system used.

Comparison of These Thermal Degradations with Previously Reported Studies. The trends observed here for the polyester degradation are in good agreement with Brauman's results¹⁰ for the degradation of a polyester thermoset made from orthophthalic acid, maleic acid, and propylene glycol in a molar ratio of 2:1:3 and crosslinked with 40 wt % of styrene. The early products from the isothermal degradation of the thermoset at 350°C in air were rich in phthalic

anhydride, whereas styrene, styrene oligomers, toluene, and ethylbenzene were formed mainly during the later stages of decomposition. In contrast to our results, a little benzaldehyde (~1%) was found in the products from a 30-min degradation. This difference in the results is probably a direct consequence of the larger gas flow (~12 times) used by Brauman in her furnace system. Unfortunately, the other pyrolysis-gas liquid chromatography studies that have been carried out yield only a limited amount of information regarding the degradation mechanism. Luce and co workers,¹⁷ when developing a method for characterizing isophthalate based polyesters, found that the maximum number of volatile breakdown products arose at pyrolysis temperatures of ~650°C. Of over 30 products, only benzene, toluene, and styrene were identified. Belinski and co-workers¹⁸ pyrolyzed polyesters made from maleic anhydride, succinic anhydride, diethylene glycol, and styrene on a platinum filament at 550°C and 750°C in a stream of helium. They identified styrene, toluene, maleic anhydride, succinic anhydride, carbon monoxide, and carbon dioxide in the breakdown products and showed that the ratio of the latter two gases was a function of the degradation temperature and polymer structure. Vijayakumar and Fink²⁵ used gas liquid chromatography-mass spectrometry to examine the effect of HET acid (1,4,5,6,7,7-hexachloro-5-norbornene 2,3-dicarboxylic acid) content on the mass distribution of the high vacuum isothermal pyrolysis products from polyesters made from fumaric acid, phthalic acid, HET acid, and 1,4-butanediol. The aromatic compounds of benzene, styrene, toluene, and ethylbenzene constituted ~60–80% of the total pyrolysis products—benzene contributing between 2% and 7% of the total. Other products reported included butadiene, tetrahydrofuran maleic anhydride, and hexachlorocyclopentadiene. Rather surprisingly, no phthalic anhydride was found. It was assumed that the benzene was produced only from the phthalic anhydride units in the chain and not from the styrene units. The hexachlorocyclopentadiene, formed from a reverse Diels-Alder reaction of the HET acid units present in the polyester chain, acted as a chain transfer agent interfering with the unzipping reaction of the styrene crosslinks. Many degradation products, including several polycyclic aromatics, were identified by Green, Hume, and Kumar²⁴ in their studies which showed that there was a correlation between the yields of the volatile aromatics and smoke formation. Unfortunately, the pyrolysis was carried out in an inert atmosphere at relatively high temperatures so that the results do not lend themselves to a direct comparison with the results reported here.

Despite the fact that Brauman's investigations¹⁰ indicate that the polyester made from orthophthalic acid, maleic acid, propylene glycol, and styrene has a low susceptibility to oxidative degradation, we hesitated in making too much of direct comparisons between the pyrolysis studies carried out in high vacuum or inert atmospheres and our degradation studies in air. Clearly, there are many products common to the different degradation studies, but more work is needed before the effects of the different modes of degradation on the product profile are understood.

Implications Regarding the Mechanism of the Thermal Degradation of Polyester Thermosets. Regarding the actual mechanism of thermal degradation of polyester thermosets, Ritchie¹⁶ concluded when studying polyethylene fumarate crosslinked with methyl methacrylate that depolymerization of the crosslinking chains occurred prior to the disruption of the polyester chains.

Anderson and Freeman⁴ found that polyesters prepared from maleic anhydride, phthalic anhydride, propylene glycol, and styrene degraded in air in four stages. The first stage occurred over a temperature range of 200–300°C and was shown by DTA to be associated with an exothermic process. Since benzaldehyde was identified in the volatile degradation products corresponding to this temperature range, they proposed a mechanism which involved preliminary oxidation at the α -carbon of the styrenated branches followed by rearrangement, cleavage, and hydrogen transfer to yield benzaldehyde and an alkene residue on the main polymer chain. The two subsequent endothermic reactions (300–420°C) were attributed to bond rupture and release of phthalic anhydride and other products by a free radical mechanism. The final exothermic process (450–550°C) was attributed to the combustion of the carbon residues.

Moore and his associates^{5–7} extended the studies of Anderson and Freeman⁴ to a poly(propylene–maleate) and to a poly(propylene–maleate–phthalate) of high reactivity (0.7 mol maleic:0.3 mol phthalic), in conjunction with amounts of styrene varying from 0% to 50%. The thermogravimetric results were very similar to those of Anderson and Freeman for the styrenated poly(propylene–maleate–phthalate). They observed that increasing the styrene content of the poly(propylene–maleate) system resulted in a smaller initial degradation stage occurring at a higher temperature. They attributed this to a transfer of oxidative attack from the main chain, as the number of double bonds is reduced, to the α -carbon atoms of the styrene units. In direct contrast to this, Takaoka, Mihara, and Mihara⁸ found when studying similar polyester thermosets to those used by Anderson and Freeman that the first weight loss in vacuum was due to phthalic anhydride.

Our studies indicate that phthalic anhydride is lost in the first stage of the degradation of the polyesters made from maleic anhydride, phthalic anhydride, NPG/DBNPG, and styrene. It would appear that preliminary degradation occurs in the main chain here since no benzaldehyde was detected in the early degradation products and only small quantities of styrene. Our results are in agreement with those of Brauman¹⁰ but not with those of Anderson and Freeman⁴ and Moore and co-workers.^{5–7} The only difference in the polyesters studied was that, instead of using propylene glycol as the glycol component, we used neopentyl glycol and dibromoneopentyl glycol.

The variations in the product distributions obtained are probably due to the differences in the conditions under which the degradations occurred and not to changes in the polymer structure. Here, as a result of the low flow rates of air used in the furnace, degradations occurred in an oxygen deficient atmosphere. Hence they were more akin to thermal, rather than thermooxidative, degradations. If this assumption is correct then the weakest point in the structure of the thermoset would appear to be at the phthalate ester units in the main chains, with the expulsion of the phthalic anhydride then being a rather facile process. In the presence of oxygen attack at the α -carbon of the styrene units becomes a competing reaction. What is perhaps surprising is that no phthalic anhydride was observed in the low temperature degradation products obtained by Anderson and Freeman. It must be remembered though that their deductions were based on the infrared analysis of the product mixtures, as opposed to the actual identification of the products as was done here. Clearly more extensive investigations need to be conducted before the mode of degradation can be stated with any degree of certainty.

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