The effects of structure on the thermal degradation of polyester resins

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Abstract

Thermal methods have been used to study the stability and the stages of degradation of unsaturated polyester resins of various structures. The effects of altering the glycol or the aromatic acid and of introducing particular structural units have been investigated. Thermal analysis results are presented for each type of structure and conclusions deduced on the structures likely to be the most stable.

Keywords: Polyester resins; Polymer structure; Thermal degradation; Thermogravimetry

1. Introduction

The widespread use of polyester resins, especially when reinforced with glass fibre supports an important moulding and construction industry. The properties of the resins may be varied by altering the monomers used and this has allowed applications for these resins to continue to develop.

The basic polyester, made by reacting a glycol, an unsaturated dibasic acid or anhydride, and a saturated or aromatic diacid or anhydride and then cross-linking with styrene, has the great disadvantage of high flammability. Although this may be combated by the use of flame-retarding monomers and additives [1–3], it is important to know the most likely mode of decomposition and the effects of using different monomers on the stability of the resins. By varying the monomers, the structural reasons for the alteration in stability may be investigated.

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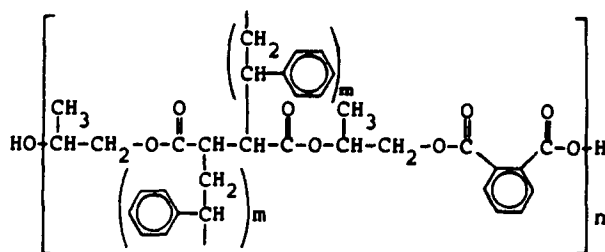
The effects of structure on stability were investigated by Pohl [4] who concluded that the introduction of –COO– groups into the chain considerably reduces the thermal stability. He also suggested that their degradation involves random chain cracking to smaller molecules.

Many of the investigations of thermal stability have been carried out using thermal methods, especially thermogravimetry (TG) and differential thermal analysis (DTA). Thermomechanical, thermoptical and evolved gas techniques have been used as complementary methods to study changes in properties and degradation products.

Extensive studies of the degradation of linear polyesters such as poly(ethylene terephthalate), PET, have been reviewed by Zimmermann [5]. The initial step of the thermal degradation is a first-order reaction involving random scission of the chain at an ester link. This results in the formation of a vinyl ester end-group and a carboxyl end-group. The thermooxidative process starts by the formation of a hydroperoxide at a methylene group. The effects of temperature, of metal catalysts and of structural modification on the thermal and thermooxidative degradations and the kinetics of the reactions are discussed, and the value of results obtained from thermoanalytical methods is stressed. The exothermic effects shown by DTA prior to the melting endotherm show that the thermooxidative reaction occurs even in the solid state.

Miller [6] used TG and DTA to compare the thermal stabilities of PET and polycarbonate and Vijayakumar and Fink [7] studied both PET and poly(butylene terephthalate), PBT, by thermal analysis and identified products of pyrolysis by mass spectrometry. These papers report the start of exothermic decomposition in air at about 400°C for PET and PBT.

Anderson and Freeman [8] used TG and DTA to demonstrate that a resin made from propylene glycol–maleic anhydride–phthalic anhydride and cross-linked with 30% styrene (Fig. 1) began to decompose in air at about 200°C, and had lost 87% of its weight by 418°C and 97% by 550°C. In argon, the decomposition followed a similar pattern, but finished by 450°C, leaving a 6% residue. DTA showed that there was an exothermic trend between 160 and 290°C followed by a large endotherm in the range of 290–490°C. They identified benzaldehyde, unsaturated hydroxy esters, phthalic an-

where m = 1 – 3
n = 10 – 30

Fig. 1. Structure of a typical polyester resin prepared from propylene glycol, maleic anhydride and phthalic anhydride and cross-linked with styrene.

hydride and low molecular weight esters of propylene glycol plus gaseous products such as carbon dioxide, methane and propene in the degradation products.

Anderson and Freeman [8] proposed a mechanism for the degradation in air involving oxidative attack at the α-carbon of the styrene, followed by rearrangement. Cleavage then occurs between the carbonyl and the α-carbon, followed by hydrogen transfer from the β-carbon to the benzoyl radical. This accounted for the exothermic first stage in air. The endothermic second and third stages were attributed to bond cleavage and the elimination of phthalic anhydride, plus the formation of hydroxyesters. In air, exothermic oxidation of the char gave the final stage.

Thermogravimetric and isothermal weight loss experiments by Vinogradova et al. [9] on polyesters made from phenolphthalein, fumaric and terephthalic acids, with a molecular weight range of 3000–30000 showed that the start of degradation was little affected by molecular weight, but that in the later stages, the higher molecular weight materials lost less weight.

Moore and co-workers [10, 11] compared the TG and DTG results for the thermal degradation of propylene glycol–maleic anhydride (PG/MA) and propylene glycol–maleic anhydride–phthalic anhydride (PG/MA/PA) systems with the same mixtures cured with styrene contents between 20 and 40%. The isothermal weight loss at 250°C decreased rapidly for both systems at first, but for the styrenated system the loss was reduced in the early stages and increased in the later stages.

It has been shown by Skinner et al. [12] that the degradation of a neopentyl glycol–maleic anhydride–phthalic anhydride resin cross-linked with styrene involved three stages in air. Pyrolysis studies clearly indicated that phthalic anhydride is lost in the earliest stages and continues to be lost, together with styrene and a complex mixture of products during later stages. This is in agreement with Brauman [13].

2. Experimental

2.1. Preparation of the polyester resins

Three series of resins were prepared, all containing glycol, maleic anhydride and benzene dicarboxylic acid units and cross-linked with styrene.

2.1.1. The glycol series (Table 1A)

These resins were prepared using either a straight chain or a branched glycol, maleic anhydride and phthalic anhydride in the molar ratio 2.2:1:1, plus 100 ppm of m-tertiary butyl hydroquinone (MTBH) as an inhibitor to prevent the maleic anhydride cross-linking. These monomers were heated under nitrogen in a 1 dm^3 flange pot for one hour at 175°C and then at 190°C with increased nitrogen flow. The water was removed in a Dean and Stark trap until the acid number reached 30–40. Samples were removed for spectroscopic analysis at this stage. After cooling to 60°C, styrene was added to give 35% styrene by weight in the final mix.

The resins were cured by the addition of 2% cobalt naphthenate accelerator (as 6% styrene solution) and 4% methyl ethyl ketone peroxide catalyst. This gave the optimum gel time of about 45 min. The resin was then cast either as a thin sheet between Melinex

films or as small blocks in silicone rubber moulds and cured for 24 h at room
temperature followed by 3 h in an oven at 80°C.

2.1.2. The acid series (Table 1B)

Here the phthalic acid resin was made as in the glycol series, but the others were
made using propylene glycol, maleic anhydride and either isophthalic acid or tereph-
thalic acid. Due to the different reactivities, these resins required a two-stage condensa-
tion. In the first stage, propylene glycol (2.2 mol) and the aromatic diacid (1.0 mol) were
heated under nitrogen in a 1 dm^3 flange pot fitted with a condenser having its jacket
heated to 90°C to ensure the removal of water but the retention of the glycol. Heating
was continued until an acid number of 10 was reached. In the case of the terephthalic
acid, tin(II) oxalate (0.2% of the initial charge weight) and sodium acetate (0.06% of the
initial charge weight) were added at the start as catalysts. The mixture was then cooled
to 125°C and the maleic anhydride (1.0 mol) added together with MTBH as inhibitor.
The condenser was replaced by the Dean and Stark assembly and the temperature of
the mixture raised rapidly to $\approx$ 200°C. The condensation was continued to an acid
number of 30–40. Addition of styrene and curing were then carried out as above.

2.1.3. A miscellaneous series (Table 1C)

Several resins were synthesised to test aspects of the structure–stability relationship.
These were generally made by the single-stage process given in section 2.1.1.

The Crystic 196 resin (Scott Bader Ltd.) is a typical commercial resin made from
mixed ethylene and propylene glycols, maleic and phthalic anhydrides and cross-linked
with styrene.

2.2. Spectroscopic examination of structure

2.2.1. NMR

Polyester resin mixtures, before the addition of styrene, were characterised by NMR
spectrometry. Small samples were dissolved in d-6 propanone with tetramethylsilane
(TMS) as internal standard. Both proton and carbon-13 NMR spectra were obtained
on these solutions using a Bruker WP80 FT-NMR.

2.2.2. IR

Infrared spectra were obtained for the resins by drawing a KBr disc through a drop
of the uncured resin mix on a Melinex film and smearing this out across about 10 cm of
clean Melinex. This gave a sufficiently thin film for good spectra and for the infrared
spectra to be measured during curing using a Perkin-Elmer 782 IR spectrometer.

2.3. Thermal analysis

2.3.1. Thermogravimetry (TG)

It was shown that similar thermal analysis curves were obtained using either small
flakes from a thin sheet or finely ground material. Samples of about 10 mg were heated
in a platinum crucible on a Stanton Redcroft TG 770 thermobalance at 15°C min^{-1} in

a gas flow of air or nitrogen of 3 cm^3 min^{-1}. The derivative thermogravimetric (DTG) curve was calculated electronically and the curves for temperature, weight and DTG recorded on a Linseis 3-pen recorder. Results were generally averaged over five replicates.

2.3.2. Differential thermal analysis (DTA)

Examination of some resins by DTA was carried out using samples of 10–30 mg diluted with alumina and contained in a platinum crucible. The reference material was also alumina and both sample and reference were heated in a Stanton Redcroft DTA 673 at 15°C min^{-1} in a gas flow of air or nitrogen of 100 cm^3 min^{-1}.

3. Results and discussion

3.1. Spectra

The polyester resins may be considered in the groups listed in Tables 1A–C. For the precursor, before the addition of styrene, the ^{1}H and ^{13}C NMR were determined. Despite the rather broad peaks obtained, due to the polymeric nature of the materials, a reasonable assignment of the peaks may be made, although the integration values were somewhat variable. A typical proton NMR spectrum, shown in Fig. 2 for·P2MI (see Table 1B), clearly shows the aromatic disubstitution pattern, in this case meta, in the region $\delta = 7.4$–8.8 ppm. The partial conversion of the maleate structures ($\delta = 6.3$) to the isomeric fumarate structure ($\delta = 6.8$) is also evident. The aliphatic glycol hydrogens show up at $\delta = 1.2$, 4.3 and 5.5 ppm. The values of some of the integrals are higher than expected, perhaps due to some entrained water.

The carbon-13 NMR shown in Fig. 3 supports the structure proposed. Peaks due to the aromatic carbons show at around $\delta = 135$ ppm, for the alkenyl carbons at $\delta = 130$ ppm and for the aliphatic carbons at $\delta = 15$, 61 and 70 ppm. All are clearly defined. The two different ester carbonyls gave a close doublet peak near $\delta = 165$ ppm.

The maleate/fumarate ratios determined from the proton NMR are quite variable, as shown in Table 2.

The infrared spectra of the majority of the resins were very similar, showing, as in Fig. 4, the typical bands for the proposed structures. Exceptionally, the ether-linked glycol resins showed a C–O stretch at 1070–1150 cm^{-1}. It was possible to study the cure of the resins by following the changes in the infrared spectra, particularly the disappearance of the –CH=CH$_2$ vinyl peaks from the spectrum.

3.2. Thermal analysis

Thermal analysis results were most informative in the studies of the stability and the stages of degradation of the resins. The onset temperatures are reported for the loss of the first 1%, but may not be significant due to the loss of small quantities of dimethyl phthalate present in the solvent for the catalyst.

Table 1
The polyester resins studied

Table 1A: Glycol series

A.1: Straight chain	Polyester Code
1,2-Ethanediol (ethylene glycol)	EMP
1,3-Propanediol	PMP
1,4-Butanediol	BMP
1,6-Hexanediol	HMP

A.2: Branched chain

1,2-Propanediol (propylene glycol)	P2MP
1,3-Butanediol	B3MP
2,2-Dimethyl-1,3-propanediol (neopentyl glycol)	NMP

Table 1B: Aromatic diacids

Phthalic anhydride	P2MP
Isophthalic acid	P2MI
Terephthalic acid	P2MT

Table 1C: Miscellaneous resins
C.1:   Ether glycols with maleic and phthalic anhydrides

3-Oxapentane-1,5-diol (diethylene glycol)	DMP
3,6-Dioxaoctane-1,8-diol (triethylene glycol)	TMP

C.2: Maleate ester

Diethylene glycol maleate	DM
C.3: Neopentyl glycol/maleic/isophthalic	NMI
C.4: General purpose commercial resin	Crystic 196

For the straight chain glycol resins, the TG curves were similar to those shown in Fig. 5a. In nitrogen, decomposition commences at about 190°C and a loss of around 7% occurs by 300°C, generally with a DTG peak near 240°C. The major degradation, with loss of more than 80% of the original mass, occurs by 500°C with a DTG peak near 410°C, often with an indistinct shoulder. The residual char was stable to 600 °C. In air, the pattern is similar, but the temperatures of the peaks are generally 5–10°C lower. The final major oxidation step in air occurs before 600°C. These results are similar to those in the literature [4, 8].

Comparing the polyesters from branched chain glycols, there is a more pronounced separation of the major peak into a doublet when run in nitrogen, as shown in Fig. 5b. Thermogravimetric data are reported in Tables 3A.1 and 3A.2. It should be noted that the average relative standard deviation for the weight losses is about 0.6. The DTA curves in Figs. 5c and d also show these stages, with a major endotherm around 400°C
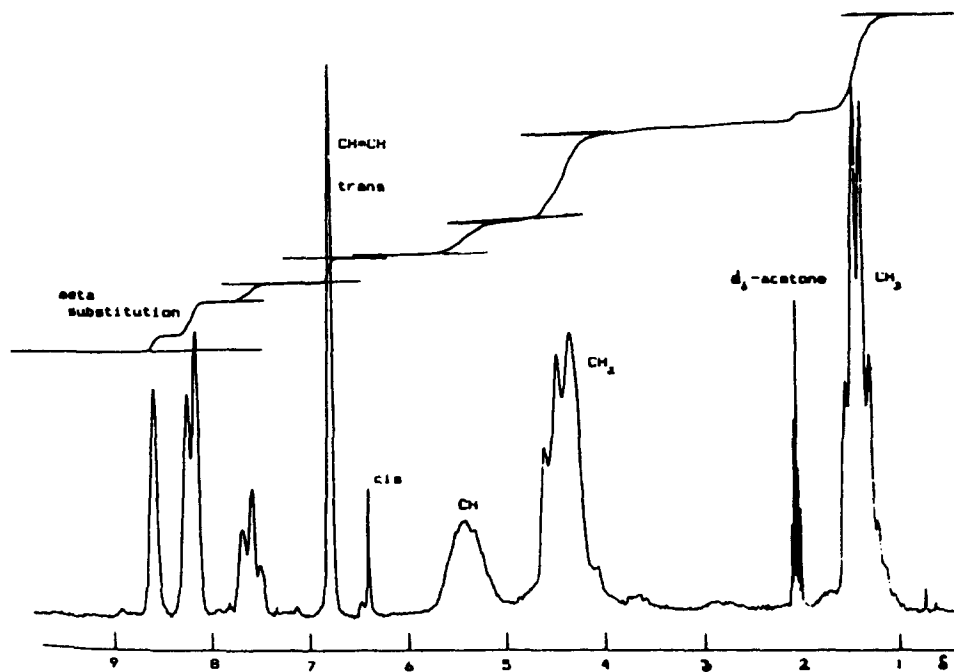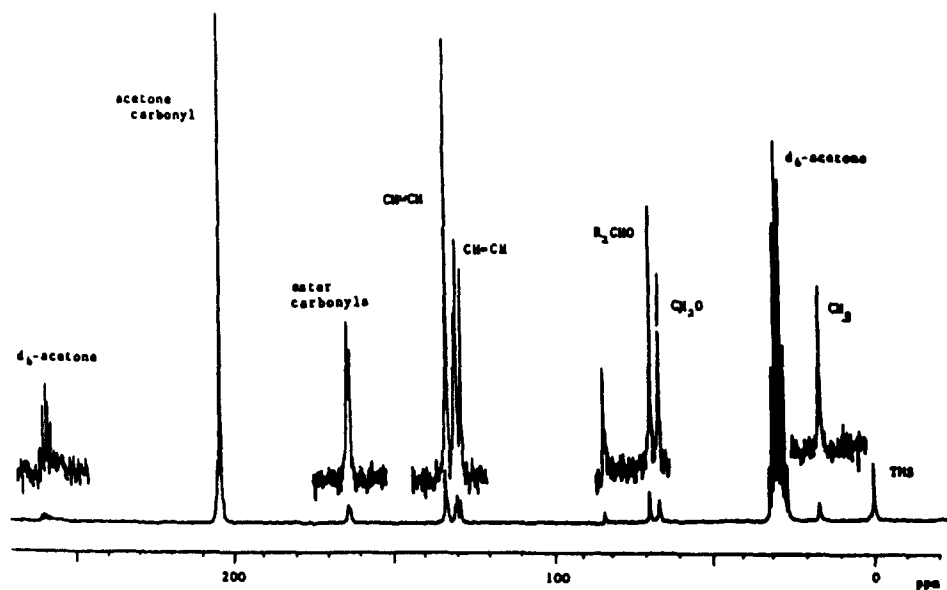
Fig. 2. Proton NMR of P2MI without styrene.

Fig. 3. Carbon-13 NMR of P2MI without styrene.

Table 2
Maleate/fumarate ratios from ¹H NMR

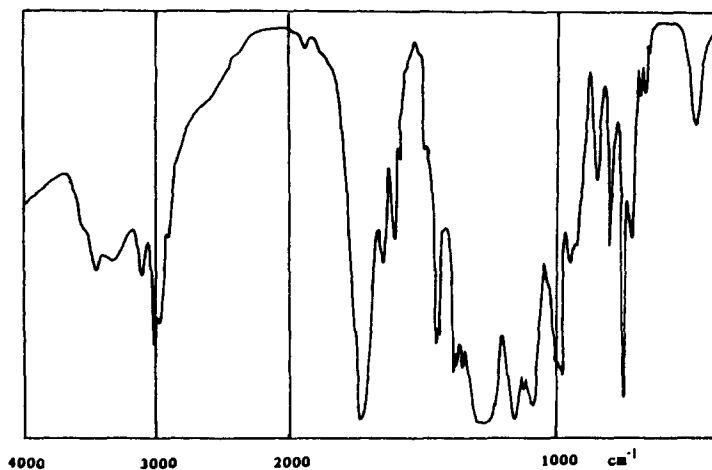| 2A Glycols		2B Acids		2C Miscellaneous	
Code	Ratio	Code	Ratio	Code	Ratio
EMP	2.33	P2MP	0.00	DMP	1.00
PMP	0.82	P2MI	7.00	TMP	1.00
HMP	0.82	P2MT	2.50	DM	2.33
				NMI	1.38

Fig. 4. Infrared spectrum of P2MI.

in both air and nitrogen and a very large exotherm between 450 and 600°C for the final oxidation in air.

The changes brought about by changing the aromatic diacid are shown in Fig. 6a–c and tabulated in Table 3B.

Both the iso- and terephthalate esters showed no evidence of the first DTG peak, which would be expected since this has been shown to be due to the elimination of phthalic anhydride [2, 13]. The final char oxidation temperatures are much the same as those for the other esters which would suggest that the mechanism of char formation and the char structures are similar for all the esters.

The DTA curve for P2MP with *o*-phthalic acid, Fig. 6d, shows a major endotherm around 400°C, which is partly due to the elimination of phthalic anhydride. The iso- and terephthalate DTA curves of Figs. 6e and f have much smaller endotherms, which are partly obscured by the large oxidation exotherm in air.

The similarity of the iso-and terephthalate ester behaviour compared to that reported for the linear polyesters [7–9] is indicative of the high stability conferred by
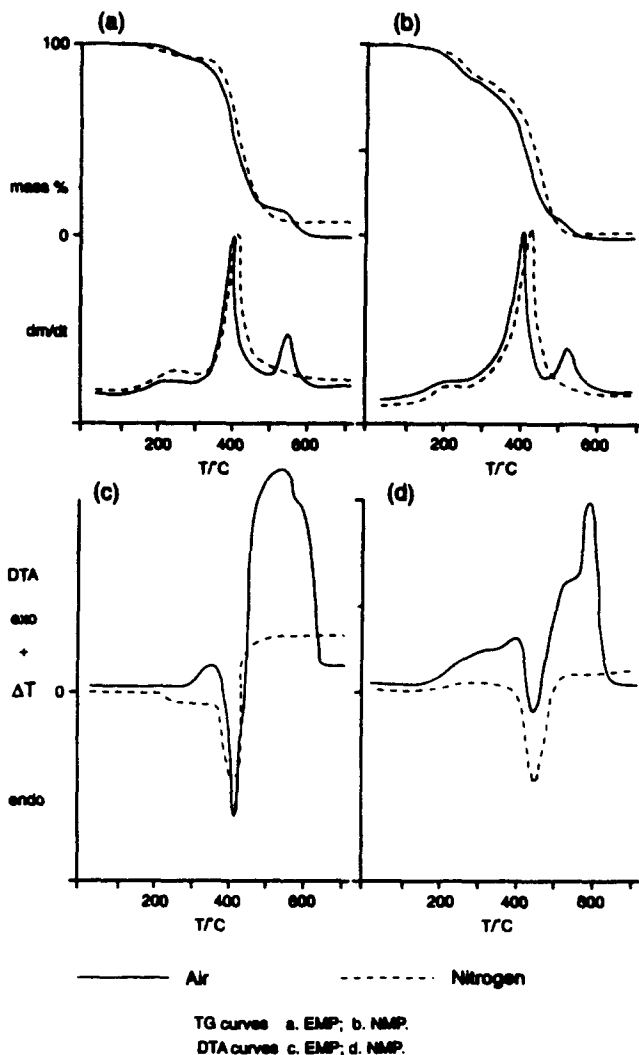
Fig. 5. Thermal analysis curves for the glycol series A polyester resins.

m-and p-dicarboxylic acids. It may also indicate that the release of styrene does not occur until the structure has been broken by scission of the ester links.

The DMP resins were unusually stable in air. Both the initial and the main weight loss peaks occurred at higher temperatures in air than in nitrogen. In contrast, the TMP resin showed the more normal results of lower degradation temperatures in air. The diethylene glycol resin without phthalic anhydride, coded DM, showed a similar three-stage degradation with Stage 1 being more stable in air, while Stage 2 is less stable in air. As Moore and coworkers [10, 11] showed, the three-component resin is somewhat more stable.

Table 3
Thermogravimetric results for the resins. Note: in all tables, results for <u>air</u> above, results for <u>N$_2$</u>, below

| | | Temperature/°C (Loss%) | | |
| | | Stage 1 | Stage 2 | Stage 3 |
Code	Onset			
<u>A.1: Straight chain glycols</u>				
EMP(air)	189	232(7.0)	407(82.6)	542(9.2)
(N$_2$)	187	236(7.0)	415(85.8)	6.6% residue
PMP	176	246(9.2)	402(85.8)	544 (5.0)
	190	251(9.2)	416(87.5)	2.4%
BMP	195	238(6.8)	413(87.5)	542(5.7)
	193	241(6.8)	420(90.9)	2.3%
HMP	172	234(8.7)	417(85.5)	542(5.8)
	182	240(9.2)	425(89.8)	1.2%
<u>A.2: Branched chain glycols</u>				
P2MP	175	215(4.6)	353(85.0)	557(8.9)
	172	214(5.3)	370(90.8)	3.5%
B3MP	225	227(3.3)	353(88.7)	536(8.0)
	220	229(3.7)	359(92.7)	3.7%
NMP	145	240(15.5)	408(77.4)	530(7.1)
	158	246(13.9)	426(81.5)	4.6%
<u>Table 3B Acid series</u>				
P2MP	175	215(4.6)	353(85.0)	557(8.9)
	172	214(5.3)	370(90.8)	3.5%
P2MI	204		388(91.7)	532(8.3)
	221		392(97.1)	2.9%
P2MT	216		387(89.7)	542(10.3)
	328		393(95.6)	4.4%
<u>Table 3C Miscellaneous polyesters</u>				
DMP	179	230(10.5)	425(77.8)	528(10.5)
	192	227(9.3)	417(83.7)	6.8%
TMP	169	212(11.1)	391(81.0)	472(8.0)
	172	265(6.4)	397(81.3)	5.1%
DM	118	201(11.1)	395(78.7)	557(10.2)
	127	195(10.3)	405(83.8)	5.9%
NMI	199	222(3.3)	430(86.6)	566(10.2)
	190	230(4.0)	439(91.0)	5.0%
Crystic	206	233(5.6)	387(87.2)	540(7.2)
196	203	236(5.0)	393(93.1)	1.9%
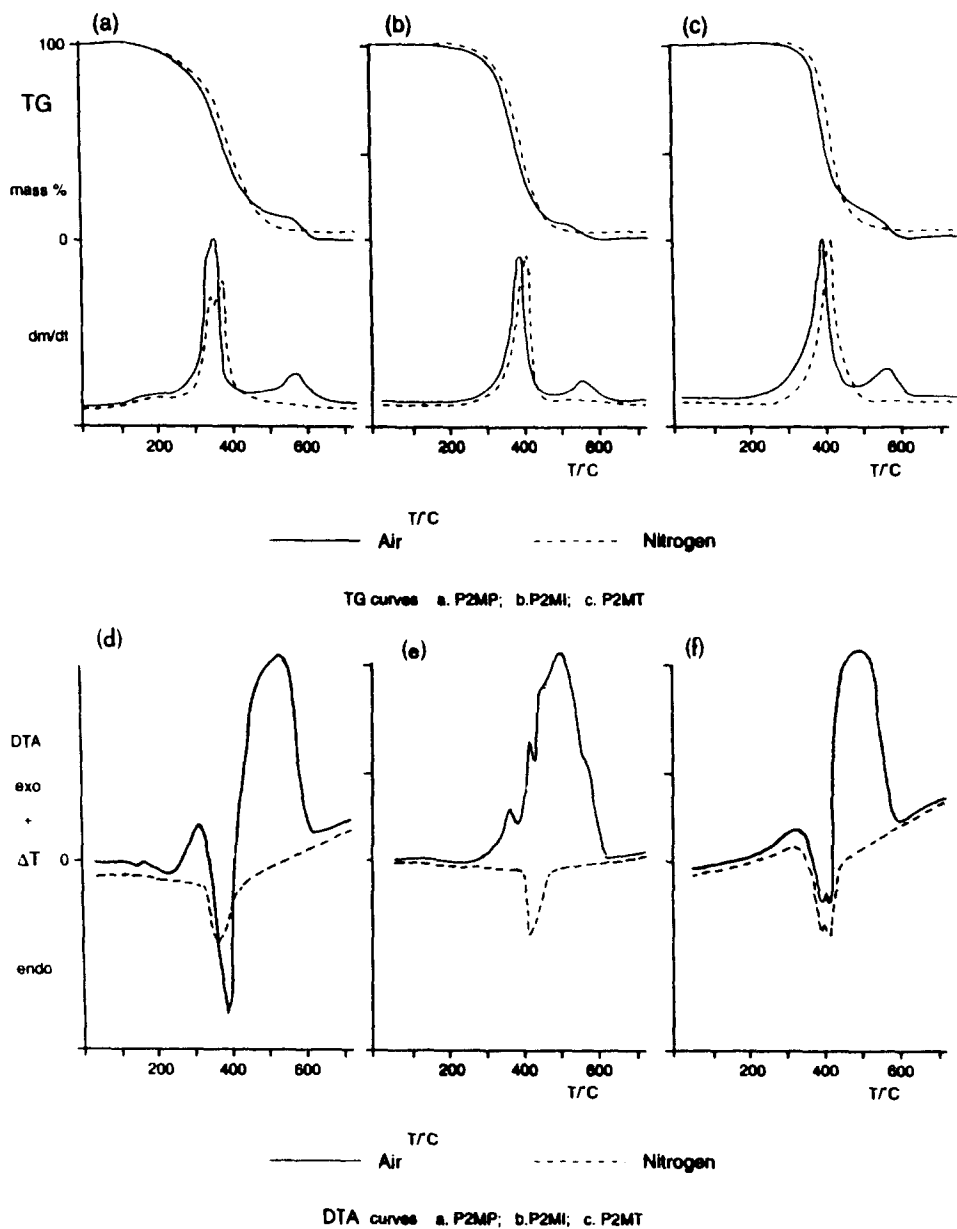
Fig. 6. Thermal analysis curves for the acid series B polyester resins.

In order to test whether a resin containing neither β-hydrogens nor phthalic anhydride would be more stable, the neopentyl glycol–maleic–isophthalic resin (cross-linked with styrene) (NMI) was tested. Fig. 7 shows that it degraded in three stages in air and two in nitrogen, and the temperature of the main degradation peak was the
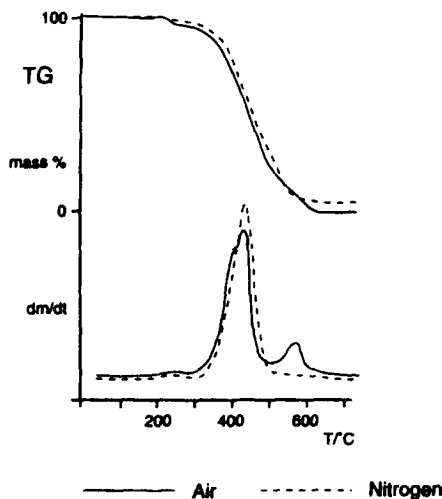
Fig. 7. Thermal analysis curves for the NMI polyester resin.

highest of all the resins investigated. This suggests that the absence of β-hydrogens and of o-phthalate structures would give added stability.

4. Conclusions

From the TG and DTA results, it is possible to make the following general comparisons. All the resins start to degrade at about 200°C, but the major weight losses occur around 400°C. Considering the effects of structural changes on this main loss, it is evident that, in general:

(i) Stability is increased with the length of the carbon chain of the glycol.

(ii) Polyesters based on straight chain glycols are more stable than those based on glycols containing a methyl substituent. The stability was increased if the glycol did not have any β-hydrogens, for example 2,2-dimethyl-1,3-propanediol.

(iii) Replacement of the o-phthalic structure with iso- or terephthalic structures altered the degradation stages and increased the thermal stability of the thermoset.

Acknowledgements

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