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Analysis of comonomer content and cyclic oligomers of poly(ethylene terephthalate)

B.J. Holland, J.N. Hay*

Plastic Materials Laboratory, School of Metallurgy and Materials, The University of Birmingham, P.O. Box 363, Edgbaston, Birmingham B15 2TT, UK

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Abstract

The concentrations of diethylene glycol (DEG) and isophthalate (IPA) units present in two commercial polyesters were measured using Fourier transform infrared (FTIR) spectroscopy and by a lowering of the melting point as measured by differential scanning calorimetric (DSC) method. To carry out the FTIR spectroscopic analysis, it was necessary to synthesise poly(diethylene glycol terephthalate) and poly(ethylene isophthalate). With FTIR spectroscopy, it was possible to measure with reasonable accuracy the DEG content of the two commercial polyesters, whereas by DSC, the presence of IPA in one material affected the results. Cyclic oligomers of the two commercial polyesters were extracted using chloroform and analysed by preparative high performance liquid chromatography and electrospray mass spectrometry. It was found that polymer containing more DEG units promoted the formation of oligomers less than trimer in size, whilst the polymer containing more IPA units promoted the formation of oligomers greater than trimer in size.

Keywords: Poly(ethylene terephthalate); Diethylene glycol; Isophthalic acid

1. Introduction

Comonomers, such as diethylene glycol (DEG) and isophthalic acid (IPA) are added to bottle grade poly(ethylene terephthalate) (PET) to reduce the rate of crystallisation during processing [1,2]. Crystallisation is undesirable, because it leads to the formation of large crystallites, which reduce the clarity of the product.

DEG units are a side product of the catalytic process in PET polymerisation [3–5]. Antimony is a commonly used catalyst, and typically leads to 1–2 mol% DEG, but concentrations as high as 15 mol% have been reported for other catalysts. On the other hand, IPA can be added to the reaction mixture in the desired quantity.

PET is known to contain an equilibrium concentration of cyclic oligomers [6,7]. The most abundant oligomer is the cyclic trimer, although an array of cyclic oligomers with repeat unit $(COC_6H_4COOCH_2CH_2O)_x$, where $x = 3$–13 has been reported [8], and in the same study, a second array of cyclic oligomers containing one DEG group was detected.

Concern has been expressed that changing the comonomer content of PET can adversely affect the properties of the material, and cause problems in blow-moulding. To investigate this, two commercial PET samples of different DEG and IPA content were chosen, and the amount of modification measured by Fourier transform infrared (FTIR) spectroscopy in comparison to laboratory synthesised poly(diethylene glycol terephthalate) (PDEGT) and poly(ethylene isophthalate) (PEI). The physical properties and cyclic oligomer content of the two commercial polymers were analysed.

2. Experimental

Commercial samples of PET were supplied by Eastman Chemical Company and Dupont Chemical Company Ltd, and assigned PET E and PET I, respectively. Their weight average molecular weights were found by gel permeation chromatography to be 42,700 and 36,400 g mol^{-1}, for PET E and PET I, respectively. PET I was known to contain approximately 2–4 mol% DEG and 1.3–2.6 mol% IPA. Dimethyl sulphoxide was used as a solvent. Chloroform, supplied by Aldrich Ltd, was used for extraction of low molecular weight material from PET.

Aldrich Ltd, supplied the following as standard laboratory grade reagents: dimethyl terephthalate (DMT), IPA, ethylene glycol (EG), DEG, antimony trioxide, calcium

* Corresponding author. Tel.: +44-121-414-4544; fax: +44-121-414-5232.

E-mail address: j.n.hay@bham.ac.uk (J.N. Hay).

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acetate, methanol and sulphuric acid for the synthesis of PDEGT and PEI. They were all used as received.

Infrared spectroscopy was carried out using a Nicolet 760 IR-Magna infrared spectrometer on commercial PET, PEI and PDEGT in order to confirm their structure and where applicable, comonomer content. In each case, sets of 256 scans were used.

Cyclic oligomers of the commercial PET samples, PET E and PET I, were extracted by Soxhlet extraction with chloroform, and reclaimed from the solution by rotary evaporation. The oligomers were subsequently analysed by electrospray mass spectrometry (ES MS).

The mixtures of oligomers were separated using preparative high performance liquid chromatography (HPLC) under the following conditions.

Column: lunar 5 μm pore C-18, reverse phase, 250 mm length × 4.6 mm inner diameter.
Flow: 0.2 cm^3 min^{-1}.
Solvent gradient: 0 min—100% water, followed by linear introduction of methanol over 30 min; 30–45 min—100% methanol.

Due to the difficulties associated with analysing these materials by liquid chromatography–ES MS, the individual components were collected and subsequently analysed by ES MS.

Differential scanning calorimetry (DSC) was used to analyse the DEG content of commercial PET samples, and to analyse PDEGT. The apparatus used was a Perkin Elmer DSC-2, with a 20 cm^3 min^{-1} flow of nitrogen. Experiments were carried using heating rates of from 10 to 40 °C min^{-1}.

3. Copolymer preparations

Dimethyl isophthalate (DMI) was prepared for use in the synthesis of PEI by a method adapted from Ref. [9]. IPA (10 g) was placed in a flask with 100 cm^3 of methanol and refluxed for 2 h in the presence of 4 cm^3 of concentrated sulphuric acid. On cooling, the reaction mixture was added to 100 cm^3 diethyl ether and 150 cm^3 of water, and shaken. The aqueous layer was discarded. The organic layer was rinsed with 50 cm^3 of water, 50 cm^3 of water with 15% $NaHCO_3$, and with 50 cm^3 of saturated NaCl solution. The organic layer was then dried over Na_2SO_4 for 10 min. DMI was recrystallised from methanol.

PEI was polymerised by a method adapted from Ref. [10]. DMI (9.7 g, 0.05 mol), EG (7.1 cm^3, 0.115 mol), Sb_2O_3 (0.04 g) and $Ca(OAc)_2$ (0.015 g) were placed in a 50 cm^3 round bottom flask under nitrogen. The mixture was steadily heated to 170 °C, at which point nitrogen was bubbled through the mixture, being careful that this did not result in volatilisation of the reactants. The reaction mixture should liberate MeOH at this stage, which was removed by distillation. The reaction temperature was then increased to 200 °C for 2 h, and 220 °C to liberate excess EG. The reaction mixture was then placed under vacuum at 280 °C for 3 h to facilitate the polymerisation.

During the reaction, Sb_2O_3 is reduced to Sb(0), which gave the polymer a dark appearance, when polymerisation was stopped. This was removed by dissolving PEI in hot DMSO and filtering. The PEI produced was a colourless glass-like solid.

DMT (9.7 g, 0.05 mol), DEG (12.1 cm^3, 0.115 mol), Sb_2O_3 (0.04 g) and $Ca(OAc)_2$ (0.015 g) were placed in a 50 cm^3 round bottom flask under nitrogen. Polymerisation was carried out under the conditions described earlier. The mixture yellowed during polymerisation, which was probably due to a small amount of degradation, and the reaction was not taken to high conversion. The product was washed with acetone to remove impurities. The resulting polymer was a soft, sticky, slightly yellow material, which became solid and brittle after several months.

4. Confirmation of structure of the polyesters

The structural repeat unit of PEI is shown in Fig. 1. The polymer produced was clear and colourless once all of the antimony catalyst had been removed from the sample. Its structure was confirmed by infrared spectroscopy (Fig. 2(a) and Table 1). For comparison, an infrared spectrum of PET is shown in Fig. 2(b), and assignments shown in Table 2.

The structural repeat unit of PDEGT is shown in Fig. 1. The polymer became slightly yellow during the early stages of transesterification, an indication of the early stages of degradation. For this reason, the reaction was not taken to high conversion. The polymer produced was slightly

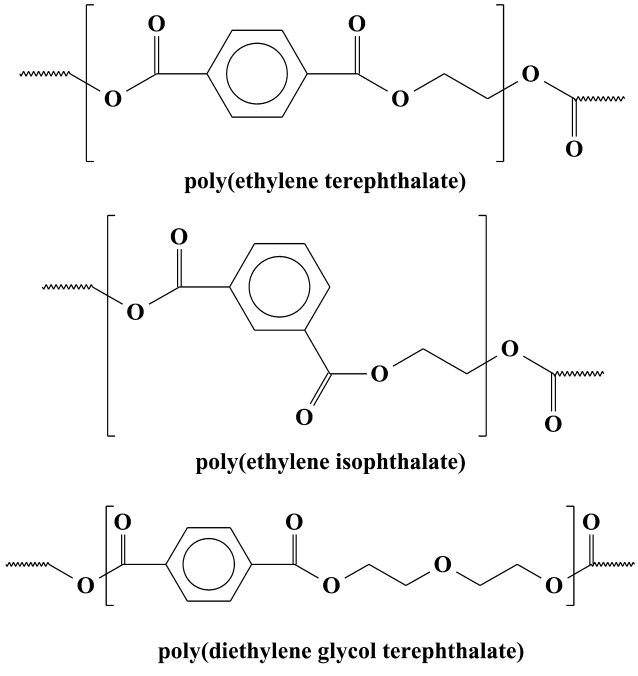

Fig. 1. Structural repeat units of PET, PEI and PDEGT.

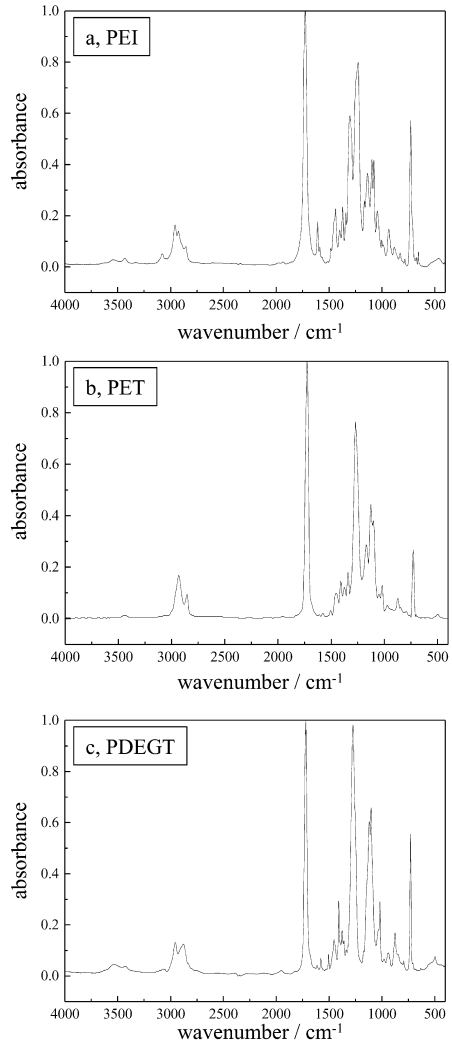

Fig. 2. (a) Infrared spectrum of PEI, (b) infrared spectrum of PET, and (c) infrared spectrum of PDEGT.

Table 1
Band assignations for the infrared spectrum of PEI [10–12]

Wavenumber (cm^{-1})	Assignment
3440	O–H stretching of EG end-group
3060	Aromatic C–H stretching
2960, 2860	Aliphatic C–H stretching
1730	Carbonyl C=O stretching
1600, 1450, 1430	Aromatic skeletal stretching bands
1465	$-CH_2-$ deformation
1295	Unknown
1220	C(O)–O stretching in ester
1165, 1090, 1070	Bands in this region are indicative of aromatic substitution pattern, and indicate 1,3-substitution
930	C–H deformation of a lone uncoupled hydrogen on an aromatic ring
820	C–H deformation of three adjacent coupled hydrogens on an aromatic ring
730	Probably associated with the out of plane deformation of two aliphatic substituents of the aromatic ring

Table 2
Band assignments for the infrared spectrum of PET [10–12]

Wavenumber (cm^{-1})	Assignment
3535	Absorbed moisture
3440	O–H stretching of DEG end-group
3060	Aromatic C–H stretching
2960, 2880	Aliphatic C–H stretching
1950	Aromatic summation band
1720	Carbonyl C=O stretching
1615, 1450, 1430, 1410	Aromatic skeletal stretching bands
1950	Aromatic summation band
1720	Carbonyl C=O stretching
1615, 1450, 1430, 1430	Aromatic skeletal stretching bands
1465	$-CH_2-$ deformation band
1270	C(O)–O stretching of ester group
1175, 1120, 1020	Bands in the skeletal ring region are indicative of aromatic substitution pattern, and indicate 1,4-substitution
980	$O-CH_2$ stretching of EG segment in PET
850	C–H deformation of two adjacent coupled hydrogens on an aromatic ring
730	Associated with the out of plane deformation of the two carbonyl substituents on the aromatic ring

yellow, clear and tacky at room temperature, although after a period of several months the material solidified and became opaque, indicative of crystallisation.

5. Analysis of commercial PET samples

PDEGT was analysed by FTIR spectroscopy, see Fig. 2(c), and assignments made in Table 3. At room temperature, the infrared spectrum of PDEGT differs from the PET samples in that it has an additional medium intensity band in the $C-H_{(str)}$ region (2880 cm^{-1}), and it was assumed that this peak was related to C–H stretching of the two middlemost methylene units of the DEG segment (Fig. 3), which is the only part of the PDEGT molecule, which differs from PET. In addition, there was a band at 940 cm^{-1}, which may have been due to $O-CH_{2(str)}$ in the DEG segment of the polymer. Furthermore, PDEGT was amorphous, and its infrared spectrum did not have the same fingerprint bands associated with the crystalline structure of PET.

It was possible to estimate the amount of DEG in PET by comparing the peak areas of the $C-H_{(str)}$ bands of PET with that of PDEGT. The $C-H_{(str)}$ band of PDEGT was deconvoluted by means of Microcal Origin 4.1 Peak Fitting Module, and the area of the band comprised of a 35% contribution from EG $C-H_{(str)}$ (2960 cm^{-1}) and a 65% contribution from DEG $C-H_{(str)}$ (2880 cm^{-1}). The area of the $C-H_{(str)}$ band, h, was divided by the area of the benzene ring breathing mode at 1405 cm^{-1}, b, in the situations of 100% DEG (h = total area) and 0% DEG (h = deconvoluted area of 2960 cm^{-1} band). These values were compared to the area of the $C-H_{(str)}$ bands of five infrared spectra of PET E and PET I, as a

Table 3
Band assignments for the infrared spectrum of PDEGT [10–12]

Wavenumber (cm^{-1})	Assignment
3535	Absorbed moisture
3440	O–H stretching of DEG end-group
3060	Aromatic C–H stretching
2960, 2880	Aliphatic C–H stretching. 2880 cm^{-1} band intense compared to that in PET, and is probably associated with an additional aliphatic C–H environment in the DEG segment
1950	Aromatic summation band
1720	Carbonyl C=O stretching
1615, 1450, 1430, 1410	Aromatic skeletal stretching bands
1580	May be associated with skeletal ring breathing, or onset of small amount of degradation during polymerisation
1465	$-CH_2-$ deformation band
1270	C(O)–O stretching of ester group
1175, 1120, 1020	Bands in the skeletal ring region are indicative of aromatic substitution pattern, and indicate 1,4-substitution
980	O–CH_2 stretching of EG segment in PET
940	Not present in PET. May be associated O–CH_2 stretching of DEG segment
870	C–H deformation of two adjacent coupled hydrogens on an aromatic ring
730	Associated with the out of plane deformation of the two carbonyl substituents on the aromatic ring

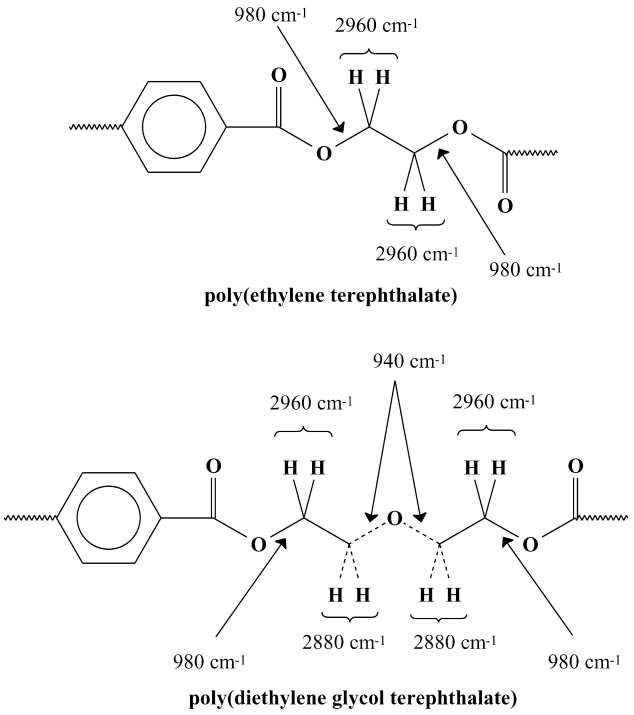

Fig. 3. Proposed causes of differences in the infrared spectra of PET and PDEGT.

ratio of the area of the corresponding band at 1405 cm^{-1} (Table 4).

Using this method, it was estimated that PET I contained approximately 3.1 ± 0.8 mol% DEG and PET E approximately 5.6 ± 1.2 mol% DEG. PET I was known to contain approximately 2–4 mol% DEG.

The infrared spectrum of PEI is fairly similar to that of PET, except between 1225 and 700 cm^{-1}, where the infrared spectrum reflects the substitution pattern of the aromatic ring (Fig. 4 and Tables 1 and 2). Many of these differences were difficult to detect at low concentration. However, one of the clearest differences could be seen below 950 cm^{-1}, where the position of $C–H_{(def)}$ deformation bands reflected the number of adjacent hydrogen atoms on the ring, due to coupling effects [13]. In PET, there is a single $C–H_{(def)}$ band, associated with two adjacent hydrogens on either side of the ring, at 870 cm^{-1}. In PEI, there are two characteristic $C–H_{(def)}$ bands, one probably associated with a lone hydrogen (930 cm^{-1}), and the other to three adjacent hydrogens (820 cm^{-1}).

From studies of thin films (approximately 5 μm), the infrared spectrum of PEI was compared to those of PET E

Table 4
Analysis of DEG content of PET from the area of the $C–H_{(str)}$ band

Sample	*h*	*b*	*h/b*	Estimated DEG content (%)
0% (calcd)	8.486	3.621	2.344	(0)
100% (calcd)	24.378	3.621	6.732	(100)
PET E	2.420	6.247	2.581	
	3.120	8.107	2.598	
	1.134	2.916	2.571	
	3.500	9.061	2.589	
	6.963	18.103	2.560	
		Average	2.588 ± 0.012	5.6 ± 1.2
PET I	5.464	13.591	2.487	
	3.244	8.052	2.482	
	4.048	10.053	2.483	
	4.734	11.689	2.4699	
	3.184	7.866	2.470	
		Average	2.479 ± 0.008	3.1 ± 0.8

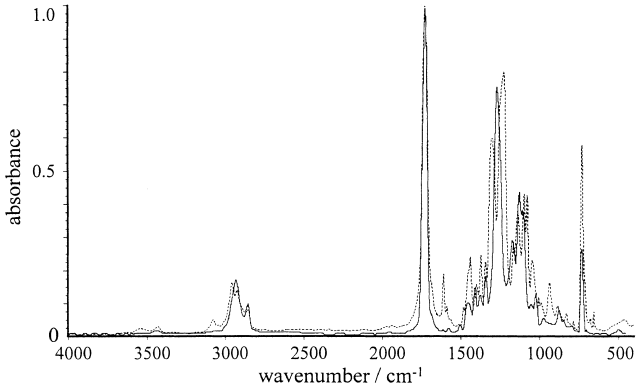

Fig. 4. Infrared spectra of PET and PEI: (—) PET, and (- - -) PEI.

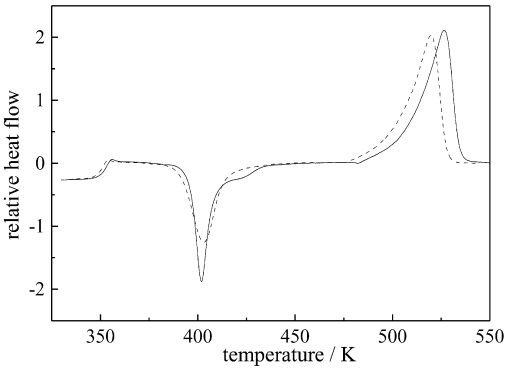

Fig. 6. DSC thermograms of amorphous quenched PET E and PET I at 10 K min^{-1}: (—) PET E, and (- - -) PEI I.

and PET I. No evidence of isophthalate units was found in the PET samples. It was considered that the low intensity of the C–$H_{(def)}$ bands limited its sensitivity. To overcome this problem, PET films of 100 μm were produced using a hot press (280 °C and 15 ton). From these films, most of the major infrared bands of PET had absorbances, which were too intense to be measured, but in the region 950–740 cm^{-1} the absorbances were less than 1.0. In the case of PET E, the infrared spectrum was that expected for PET, but in the case of PET I, a small shoulder was observed at approximately 930 cm^{-1} (Fig. 5). The assignment of this band was not absolutely clear, as it was at too high a frequency for an uncoupled C–$H_{(def)}$ band (normally 900–860 cm^{-1}), but this band was only present in PEI and not in PET, and so was likely to be associated with the isophthalate structure. In fact, it was already known that PET I contained 1.3–2.6 mol% isophthalate units, added to modify its crystallisation behaviour. It was considered that the intensities of the bands associated with isophthalate content were too low for quantitative analysis.

Samples of commercial PET (10 mg) were amorphous by quench cooling from the melt on an aluminium surface. The DSC analysis, carried out using a heating rate of 10 °C min^{-1}, is shown in Fig. 6. Both materials exhibited a glass transition and a crystallisation exotherm before melting. It was found that the glass transition temperature, T_g, of PET E was 2 °C higher than PET I. Similarly, the melting point of PET E was higher than PET I, the significance of which will be discussed later. The appearance of the cold crystallisation curve of PET was found to vary according to sample preparation and age. Therefore, few conclusions could be draw from the differences in this process for the two polymers, except PET E appeared to exhibit a shoulder on the high temperature side, which may have been due inhomogeneity in the sample, i.e. high concentrations of DEG in certain parts of the polymer. High concentrations of DEG in localised areas will affect the thermal behaviour of that portion of the polymer. Fig. 7 shows the glass transition of PDEGT, analysed by DSC at 10 °C min^{-1}. Other experiments were carried out at 20 and 40 °C min^{-1}, and the glass transition temperature, T_g, was extrapolated to zero heating rate and found to be 7 °C.

6. Analysis of comonomer content of PET by DSC

Samples of 10 mg of PET E and PET I were subjected to further DSC analysis, as described in Section 3. The crystalline melting temperatures for the samples crystallised at certain temperatures, $T_{m,x}$, were plotted against the

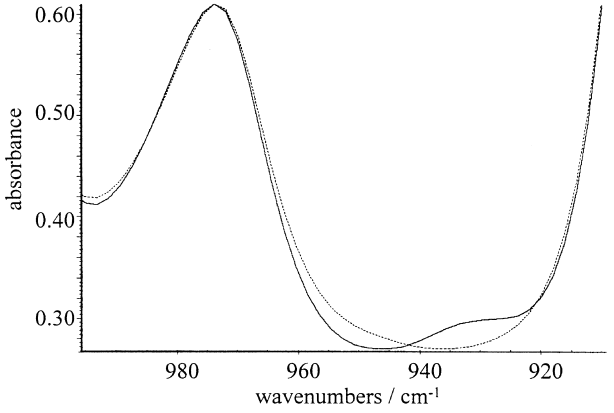

Fig. 5. Infrared spectra of PET and PEI in the fingerprint region: (—) PEI, and (- - -) PET.

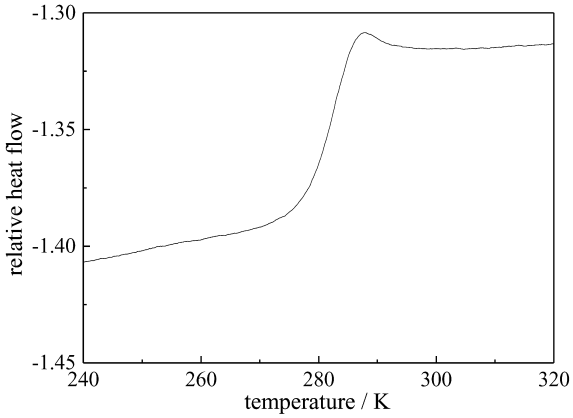

Fig. 7. Glass transition of PDEGT at 10 K min^{-1}.

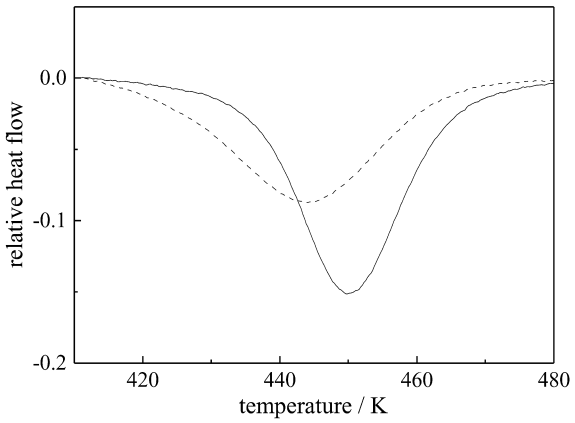

Fig. 8. Non-isothermal recrystallisation of PET E and PET I at 10 K min^{-1}: (—) PET E, and (- - -) PEI I.

crystallisation temperature, T_c. The melting point of both materials did not vary with T_c. However, according to Hoffman and Weeks [14]

$$T_m = T_{m,0}\left(1 - \frac{1}{2\beta}\right) + \frac{T_c}{2\beta}$$

where $\beta = (\sigma_e l/\sigma l_e)$ and σ is the lateral surface free energy, l is the lamellae thickness and e refers to equilibrium conditions, i.e. no annealing. For crystallisation under equilibrium conditions $\beta = 1$, hence a plot of T_m versus T_c should have a slope of 1/2. No slope was observed for PET E and PET I, which may have been due to the melting of thin crystals, followed by recrystallisation during heating to the melting point [14]. As equilibrium conditions were not observed, it was not possible to obtain the equilibrium melting point through extrapolation of the experimental data to the line $y = x$. Instead the average T_m was calculated as 256 and 247 °C, for PET E and PET I, respectively. The difference in T_m was assumed to be due to the amount and type of comonomer modifiers used in each material.

Infrared analysis of PET E showed that it was modified by DEG only. Janssen et al. [15] showed that for every mol% of DEG, the T_m of PET would drop by 3 °C, from an original value of 271 °C for 0% DEG. The T_m of PET E was 15 °C below that quoted for 0% DEG, thus PET E contained 5.0 ± 0.3 mol% DEG. This value agrees well with the 5.6 ± 1.2 mol% DEG content estimated by FTIR spectroscopy. The T_m of PET I was lower than that of PET E, although PET I was thought to contain a similar concentration of comonomer modification. For this reason, it was assumed that isophthalate units were more effective in reducing T_m than DEG units.

It was also found that samples taken from the outer and inner surfaces of the blow-moulded bottles had the same T_m as samples taken from the bulk of the material. Purification was not found to affect T_m.

The PET samples were melted and recrystallised dynamically at 10 °C min^{-1}. The results in Fig. 8 showed that both materials began to recrystallise at approximately the same temperature, although PET I subsequently recrystallised much more slowly. This was illustrated by the difference in the peak recrystallisation temperature, $T_{c,p}$, which was 176 and 170 °C, for PET E and PET I, respectively. Slow recrystallisation is desirable in bottle production, as thermal crystallisation can reduce the clarity of the final product. These results were consistent with the appearance of blow-moulded samples, which in the case of PET E showed cloudiness due to crystallisation at the base and at the screw-top of the bottle.

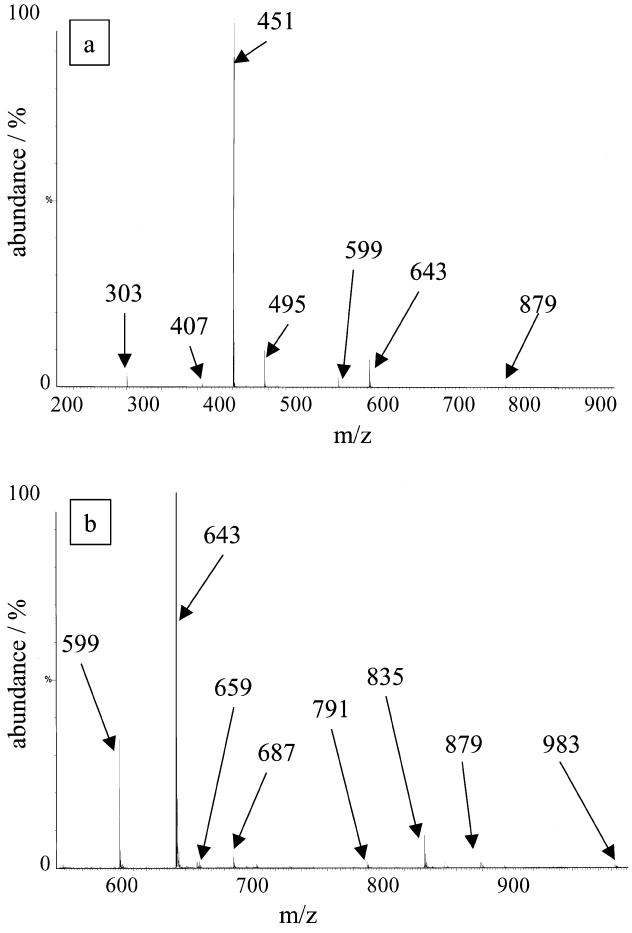

Fig. 9. ES MS spectrum of oligomers of (a) PET E, and (b) PET I.

7. Analysis of cyclic oligomers of PET by ES MS

Cyclic oligomers of PET E and PET I were extracted by Soxhlet extraction with chloroform, and obtained from solution by rotary evaporation, as described in Section 3. A yield of 0.9% (w/w) of soluble material was reclaimed from PET E, whilst PET I yielded 0.6% (w/w). The soluble material was analysed by ES MS. Typical mass spectra for PET E are shown in Fig. 9, and the peaks identified in Table 5. The mass spectrum of oligomers of PET I was found to be similar to that of PET E. The extracts were

Table 5
Assignment of ES MS mass spectrum of oligomers extracted from PET E and PET I

m/z (Da)	Intensity (%)	Assignment
303	2.5	(Cyclic monomer + two EG) + Na
407	1.0	Cyclic dimer + Na
451	100.0	(Cyclic dimer + one EG) + Na
495	10.0	(Cyclic dimer + two EG) + Na
599	2.5	Cyclic trimer + Na
643	7.3	(Cyclic trimer + one EG) + Na
659	0.1	(Cyclic trimer + one EG) + K
687	0.2	(Cyclic trimer + two EG) + Na
791	0.1	Cyclic tetramer + Na
835	0.7	(Cyclic tetramer + one EG) + Na
879	0.1	(Cyclic tetramer + two EG) + Na
983	< 0.1	Cyclic pentamer + Na

found to contain cyclic oligomers of PET with masses $192n$, $192n + 44$ and $192n + 88$, where $n = 2$–6, and a small quantity of monomer + 88. Cyclic monomer was not observed, and its production was considered unlikely due to the high strain in the ring. It was considered that the additional mass was due to additional $-CH_2CH_2O-$ groups in the oligomer, as a result of the DEG content in the polymer chains. The $192n + 44$ group of materials was the most abundant species, which indicated that the presence of DEG in the polymer chain promotes production of cyclic oligomers, due to the additional aliphatic chain segment reducing ring strain. Therefore, the higher yield of oligomers from PET E indicated that it probably contained more DEG. The lower abundance of $192n + 88$ was probably due to the probability of having two DEG units within less than six units of each other being low.

HPLC was carried out on the oligomers extracted from PET E and PET I using UV detection. Chromatograms for the oligomers of PET E and PET I are shown in Fig. 10. It was found that the extract of PET I contained all the same components as PET E, plus additional peaks of retention time 30.05, 31.20, 31.72 and 32.44 min, despite the ES MS analysis of both mixtures being similar. Preparative HPLC was carried out on the oligomers of PET I, and the eluent of each component was collected and analysed by ES MS, the results of which are shown in Table 6.

Components ranging from cyclic dimer + one EG group to cyclic tetramer + two EG groups were detected, and for both PET E and PET I cyclic trimer gave the most intense response. The three HPLC peaks that were particular to PET I had retention times of 30.05, 31.08 and 33.29 min. The molecular mass associated with the peak at 30.05 min was consistent with cyclic trimer. Cyclic trimer was also responsible for the peak at 27.93 min in the PET I trace, and it was considered that the peak at 30.05 min was an isophthalate group containing isomer of cyclic trimer. PET E contained essentially no isophthalate groups, which would explain,

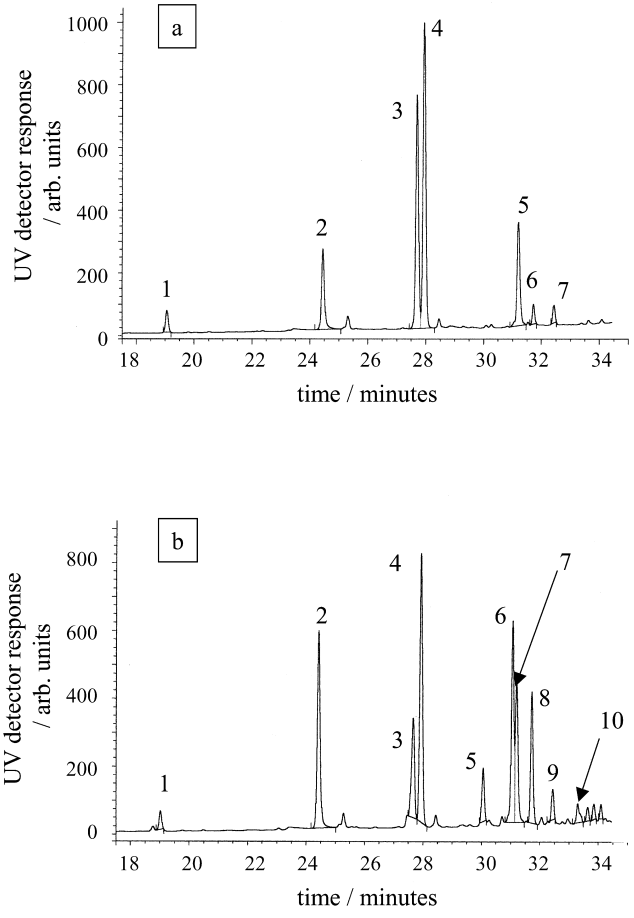

Fig. 10. HPLC chromatogram of oligomers of (a) PET E, and (b) PET I.

why the peak at 30.05 min was absent from its oligomeric mixture.

The substance responsible for the peak at 31.08 min had a molecular mass corresponding to cyclic trimer + one EG group. However, it was convoluted with a peak at 31.20 min, corresponding to cyclic trimer + 88. In PET E, only one peak is seen in this region, with a retention time of 31.20 min. This corresponds more closely with cyclic trimer + two EG groups. However, ES MS results for the unseparated material indicated that the oligomeric mixture of PET E contained a moderate amount of cyclic trimer +

Table 6
Assignment of HPLC peaks of the cylcic oligomers of PET I

Retention time (min)	*m/z*	Cyclic oligomer
24.43	451	Dimer + one EG + Na
27.68	495	Dimer + two EG + Na
27.93	599	Trimer + Na
30.05	599	Trimer + Na
31.08	643	Trimer + one EG + Na
31.20	687	Trimer + two EG + Na
31.72	835	Tetramer + one EG + Na
32.44	879	Tetramer + two EG + Na
33.29	983	Pentamer + Na

one EG, but only a trace amount of cyclic trimer + two EG groups. It was concluded that the peak at 31.20 min in the HPLC chromatogram for PET E was in fact associated with cyclic trimer + one EG group, and the difference in retention time for this peak between the two chromatograms was due to experimental error. Therefore, cyclic trimer + two EG groups is an oligomer of PET I, but not of PET E. It was considered likely that this oligomer was present by virtue of containing at least one isophthalate group, which would promote its formation through having more favourable geometry than terephthalate units.

The peak at 33.29 min had a molecular mass equivalent to cyclic pentamer. The results indicate that although PET I contained a lower mass of cyclic oligomers than PET E, PET I contained a higher proportion of cyclic oligomers greater than trimer in size than PET E. This means that although the presence of isophthalate units probably acts to promote the formation of larger cyclic oligomers, it does not promote the formation of large quantities of oligomers. PET E, which was comonomer modified with DEG was found to contain a greater mass of low molecular weight oligomers. The presence of a large quantity of DEG units in PET E may be indicative that a different catalyst to that used in PET I (antimony) was used in polymerisation, which may promote cyclic oligomer formation.

8. Potential causes of stickiness of blow-moulded PET bottles

PET E and PET I are bottle grade polyesters and are injection-moulded and subsequently blow-moulded to produce bottles for carbonated drinks. It was found that the final product made from PET E sometimes had a tacky surface, which was not related to contamination during processing. In Section 4, polyester polymers made from the two types of comonomer modifier used in PET E and PET I were evaluated, and it was found that, at room temperature, PDEGT was sticky but PEI was not. It was found in Section 5, according to FTIR spectroscopic analysis, that PET E contained 5.6 mol% DEG, whereas PET I contained only 3.1 mol%. Hence, PET E contained almost twice as much DEG than PET I. According to Senagov and Schultz [16], the DEG segments of the copolymer would be almost entirely concentrated in the amorphous regions of PET, therefore the concentration of DEG in the amorphous region was certainly much higher than 5.6 mol%. Blow-moulding produced strain-induced crystallisation and reduced the fraction of amorphous PET. If the DEG segments were rejected to the amorphous regions, blow-moulding would increase the concentration of DEG segments in the amorphous regions. Consequently, the T_g would be reduced, and if sufficient DEG segments were present, the T_g (7 °C for PDEGT) could drop below room temperature. This would make the polymer tacky. There was no evidence to suggest that the PDEGT copolymer was present on the surfaces of the bottle at higher concentration than observed in the bulk polymer.

The cyclic oligomer content of PET E and PET I has also been determined. The cyclic oligomeric mixture extracted from PET was a colourless solid powder. It was found that the yield of cyclic oligomers increased with concentration of DEG segments in the polymer. DSC results suggested that cyclic oligomer content had no effect upon the T_m of PET, although the glass transition temperature, T_g, was not measured. Although the cyclic oligomers are not sticky to touch, if they concentrated into the amorphous region of the polymer at high enough concentration, it may be possible to reduce the T_g to an extent that the polymer becomes sticky. However, it was considered that DEG content in the polymer was the primary cause.

It was also found that PET E contained a higher proportion of cyclic oligomers than PET I. It was considered that cyclic oligomer formation was promoted by the additional chain flexibility of DEG units, and also associated with catalyst choice and content. IPA units were thought to promote the formation of larger cyclic oligomers through more favourable bond angles.

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